DEPARTMENT OF CIVIL AND NATURAL RESOURCES ENGINEERING

UNIVERSITY OF CANTERBURY

Sources and transformation of nitrogen compounds in Haytons Stream, a low lying urban drainage stream in Christchurch, New Zealand

Submitted by

Fabio Cabral Silveira

Master of Engineering Student

Dr Ricardo Bello-Mendoza (Primary supervisor)

Dr Thomas A. Cochrane (Co-supervisor)

Abstract

Haytons Stream is an urban watercourse that drains Christchurch's Wigram suburb and discharges into the Heathcote/Opawaho River. Previous studies have shown levels of ammoniacal nitrogen (NH_4-N) and oxidized nitrogen (NO_X-N) in Haytons Stream to be one of the highest among Christchurch City waterways, specifically exceeding local water guidelines for toxic concentration of NH_4-N (ECan, 2007; Moores et al., 2009). High levels of ammonia and/or related nitrogen compounds can be toxic to aquatic organisms and can have a significant effect on the stream's ecological health. The contamination in Haytons stream is symptomatic of other urban streams around the country and there is thus a need to understand the principal sources and composition of urban nitrogen contamination, the fate and transport of nitrogen compounds and their interaction with the stream.

Nitrogen compounds in Haytons Stream were thus characterized through spatial and temporal field sampling in order to better understand their sources, their relationship with the mainly industrial land use and to identify stormwater management practices to deal with these types of pollutants. Eight sites along the stream were sampled under storm and baseflow conditions during the dry and wet season.

Results from sampling showed that nitrogen compounds varied in location and time along the stream. Point discharges of NH_4-N and dissolved organic nitrogen (DON) occurred at the upper and middle part of the stream. NH_4-N was found to reach toxic levels mainly in the middle part of Haytons Stream.

Five of the highest total nitrogen concentrations found at Haytons Stream had most nitrogen compounds in dissolved form (NH_4-N, DON and NO_X-N). Levels of NO_X-N were found to exceed the local guidelines in 90% of samples while ammoniacal nitrogen in some of the samples was found to be up to 8 times higher than local guidelines.

The predominant nitrogen form changes with flow conditions. During baseflow, nitrogen is mostly in its inorganic form at the upper and middle parts of Haytons and in organic form at the lower part; during stormflow, the majority of the nitrogen is in its organic form in all sections of the stream.

Nitrogen dynamics are affected by season. An increase in temperatures and sun incidence during the dry season (i.e. summer) increases biological processes rates, incrementing ammonification,

nitrification and other processes that modify the nitrogen dynamics along Haytons Stream. During the wet season (i.e. winter), rainfall dilutes the stream water, decreasing nitrogen compounds concentrations.

Overall, results showed that nitrogen concentrations increased from the upper part to the middle part of Haytons Stream and decreased from the middle to the lower part. Retention ponds along the stream together with the recently planted riparian zone and a wetland at the lower part of the catchment were found to help in the reduction of all forms of nitrogen, except particulate organic nitrogen (PON).

It can be concluded that stormwater management along Haytons stream should be focused on the dissolved forms of nitrogen. The wetland/ponds at the outlet of Haytons Stream does a good job of converting nitrogen to a predominantly particulate form of nitrogen (PON, i.e. algae), which could be removed through filtering or other physical treatment means. Further research is necessary to identify and stop point discharges at Haytons Stream and evaluate methods to mitigate PON entering Heathcote/Opawaho River.

Acknowledgements

The author wishes to express his gratitude to the following people, who significantly contributed to the outcomes of this Masters research:

My supervisors, Ricardo Bello-Mendoza and Tom Cochrane, for their support, guidance, wisdom, and constructive comments when needed throughout this project.

Technical staff at the University of Canterbury, in particular Peter McGuigan for his expert advice and help on laboratory water quality analyses.

The Department of Civil and Natural Resources Engineering for providing me with the opportunity to work as a Teaching Assistant while undertaking this Masters Project.

Environment Canterbury (ECAN) staff, in particular Michele Stevenson for support and advice regarding this project.

This research would not have been possible without the support of ECAN who provided a scholarship and the Waterways Centre for Freshwater Management who provided financial support to attend the Water Infrastructure and the Environment Conference in Queenstown.

My family and friends whose love, support, and encouragement are appreciated and truly inspiring.

I am grateful for the enthusiasm, help and support from my fellow postgrad friends, especially those who have shared an office with me.

Last but not least, I would like to thank my partner and friend Paula Denise Yarur Thys for her help during some of the sampling campaigns. Without your unconditional support this dissertation would not have come true.

Table of Contents

List of Tables

List of Figures

List of Abbreviation

CCC	Christchurch City Council
°C	Degree Celsius
NH_3	Ammonia
NH_4^+	Ammonium
NH_4-N	Sum of ammonia and ammonium; (total) ammoniacal nitrogen
NO_2^-	Nitrite
NO_3^-	Nitrate
NO_X-N	Sum of nitrite and nitrate; (total) oxidized nitrogen
DON	Dissolved organic nitrogen
PON	Particulate organic nitrogen
DIN	Dissolved inorganic nitrogen
TN	Total nitrogen
DOC	Dissolved organic carbon
g/m^3	Gram per 1 cubic meter (1000 Litres)
mg/L	Milligram per 1 Litre
ECan	Environment Canterbury
WRB	Wigram Retention Basin
%	Percentage
ANZECC	Australian and New Zealand Guidelines for Fresh and Marine Water Quality
NPS-FM	National Policy Statement for Freshwater Management (New Zealand)
NTU	Nephelometric turbidity units
µS/cm	Micro Siemens per centimetre

Research Outputs

Conferences

Presentation

Silveira, FC., Bello-Mendoza, R. and Cochrane, TA. (2015) *Assessing the source and transformation of nitrogen compounds in a low lying urban drainage stream in Christchurch (Haytons Stream).* Christchurch, New Zealand: Waterways Postgraduate Student Conference 2015, 17/11/2015.

Silveira, FC., Bello-Mendoza, R. and Cochrane, TA. (2016) *Source transformation of nitrogen compounds in Haytons stream, a low lying urban drainage system in Christchurch.* Nelson, New Zealand: Water New Zealand's Stormwater Conference 2016, 18/5/2016.

Poster

Silveira, FC., Bello-Mendoza, R. and Cochrane, TA. (2016) *Dynamics of nitrogen compounds in Haytons urban drainage stream, Christchurch*. Christchurch, New Zealand: Waterways Postgraduate Student Conference 2016, 15/11/2016. **Second prize poster**.

Silveira, FC., Bello-Mendoza, R. and Cochrane, TA. (2016) *Dynamics of Nitrogen Compounds in Haytons Stream, Christchurch*. Queenstown, New Zealand: Water Infrastructure and the Environment, 56th New Zealand Hydrological Society Conference, 28/11/2016.

1 Introduction

Nitrogen contamination is a global problem affecting both rural and urban waterways. Much of the nitrogen applied to agricultural and urban areas ultimately ends up in rivers and near shore coastal systems due to surface runoff. In agricultural areas, the sources of nitrogen include fertilizers and runoff from animals' feedlots. In urban areas, sources include organic matter, home lawn fertilizers and industrial discharges (Dalton & Brand-Hardy, 2003). Rural and urban areas can also receive nitrogen discharges from other sources such as atmospheric deposition over water surfaces, activities on land that generate contaminants (logging and wetland conversion), and development of land or waterways (Carpenter et al., 1998). Additionally, nitrogen contamination can be a product of chemical processes occurring in stormwater sumps during dry weather (Memon & Butler, 2002) or in soils in urban riparian zones (Groffman et al., 2002).

In aquatic systems, increased levels of nitrogen can often lead to hypoxia (low oxygen), altered biodiversity levels or changes in food-web structure (Vitousek et al., 1997). This may lead to changes in overall ecosystem function and recent studies suggest that alterations to the nitrogen cycle may lead to an increased risk of parasitic and infectious diseases among humans and wildlife (Johnson et al., 2010). Increases in nitrogen concentrations in aquatic systems can also lead to increased acidification, due to the nitrification process, which is detrimental to water quality (Stumm & Morgan, 1995).

In urban areas such as Christchurch, where stormwater is discharged mostly untreated directly into urban waterways, nitrogen contamination can be a significant problem. This seems to be the situation for Haytons Stream. The Haytons Stream catchment has two sub-catchments: Haytons and Paparua. It has an approximate area of 13 km^2 and it is located in the western part of Christchurch, with around 6 km^2 of residential, 4 km^2 industrial and 3 km^2 of rural land use. Its stormwater is channelled through pipelines and ends up at the Wigram Retention Basin, which then discharges to the Heathcote River (Figure 1-1).

The Paparua Stream sub catchment, on the northern side of the catchment, has rural and predominantly residential land use, covering a larger area of the catchment. According to previous water quality monitoring, the stream's water quality is good in the Paparua Stream (ECan, 2007). In the Haytons Stream sub catchment, which lies in the southeast part of the catchment, the predominant land use is industrial, which presents the potential for a wide range of contaminant sources.

Previous water quality monitoring has indicated that the levels of ammonia in Haytons Stream is the highest among all sampling sites in the Christchurch region (ECan, 2007), higher than ecological guideline values for waterways (ANZECC, 2000) and close to the toxicity concentration level for ammonia (Ministry for the Environment, 2014), which contributes to the degradation of the Heathcote River (Moores et al., 2009). However, the source of this contamination was not clear. There is a need for a better understanding of the principal sources and composition of urban nitrogen contamination, the fate and transport of nitrogen compounds and their interaction with the stream water.

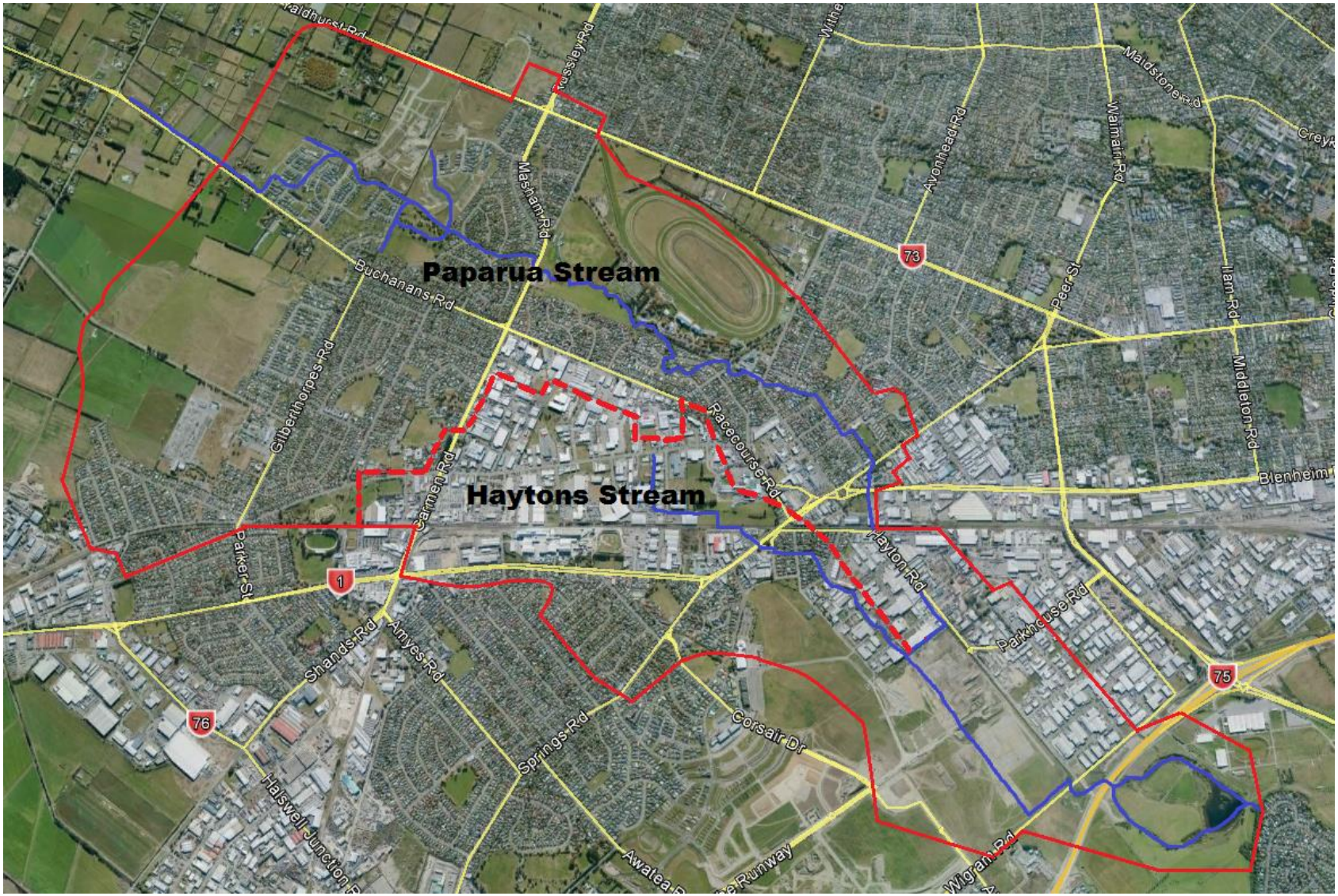


Figure 1-1: Aerial photograph of Haytons Stream catchment showing catchment boundary (solid red line), sub-catchment boundary between Paparua and Haytons Stream (dashed red line), Haytons and Paparua stream (dark blue) and land use (industrial areas are occupied by larger white/grey roofed buildings; residential are occupied by small dark grey roofs; rural areas and parks are green colour; developing areas are brown/sand colour) (www.maps.google.co.nz).

2 Literature review

2.1 Nitrogen at the global scale

Nitrogen is one of the primary nutrients critical for the survival of all living organisms. It is a necessary component of many biomolecules, including proteins, DNA, and chlorophyll. Although nitrogen is abundant in the atmosphere as nitrogen gas (N_2), it is largely inaccessible in this form to most organisms, making nitrogen a scarce resource, which often limits primary productivity in ecosystems. Only when nitrogen gas is converted into ammonia (NH_3) does it become available to primary producers such as plants (Bernhard, 2010).

In the atmosphere, nitrogen gas (78% of air composition by volume) is unreactive because of the strong bond (three electron pairs) between the nitrogen atoms. Some bacteria (associated with certain leguminosae plants) (Burns & Hardy, 1975) and certain blue-green algae are able to fix it as organic nitrogen (Allen & Arnon, 1955). Humans have also learned to fix N_2 using the Haber-Bosch process, in which N_2 is synthetically converted (at elevated pressure and temperature and in the presence of hydrogen and a suitable catalyst) into NH_3.

The synthesis of ammonia was a revolutionary step taken by humanity. The increase of the global population, food production and soil fertilization would not be possible without the gains of nitrogen as fertilizers (Dalton & Brand-Hardy, 2003; Smil, 1997). On the other hand, the extent of anthropogenic nitrogen fixation is of the same order of magnitude as that of biological N_2 fixation. Doubling the normal concentration of reactive nitrogen changed the distribution of nitrogen compounds between water, soil, atmosphere and it was among the most significant environmental changes of the 20th Century (Vitousek et al., 1997).

Additionally, fossil fuel consumption has a significant impact on the nitrogen cycle and distribution because its combustion reaction releases $NO_{x\,(g)}$ and $N_2O_{\,(g)}$ which has a role in the nitrogen cycle and also climate change (Ravishankara et al., 2009). In water, reactive nitrogen exists in different forms, including both inorganic (ammonia (NH_3), nitrate (NO_3^-), and nitrite (NO_2^-)) and organic (in its dissolved and particulate form) (Figure 2-1).

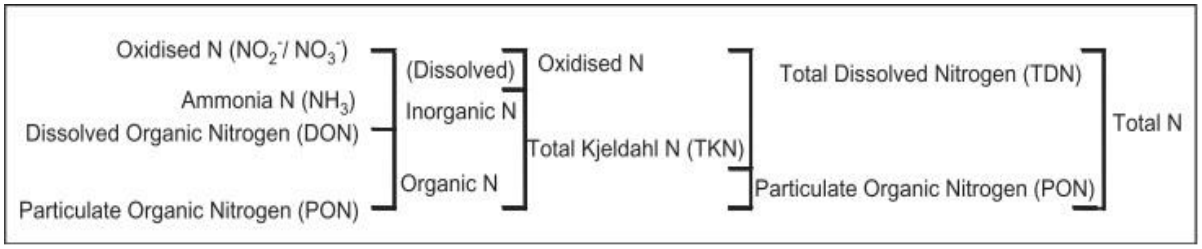


Figure 2-1: Individual constituents of total nitrogen and their named combinations (Taylor et al., 2005).

The most important processes of the nitrogen cycle in the water and soil are: uptake of nitrogen from the atmosphere (as mentioned before, called nitrogen fixation), nitrification, denitrification, anaerobic ammonium oxidation and uptake of ammonium and nitrate known as nitrogen assimilation or plant uptake (Figure 2-2).

When an organism excretes waste or dies, the nitrogen in its tissue is in the form of organic nitrogen (amino acids, DNA, etc.). Fungus and prokaryotes then decompose the tissue and release inorganic nitrogen in the ecosystem as ammonia in the process known as ammonification. The ammonia becomes available for plants and other microorganisms, during the processes of nitrogen assimilation or nitrification.

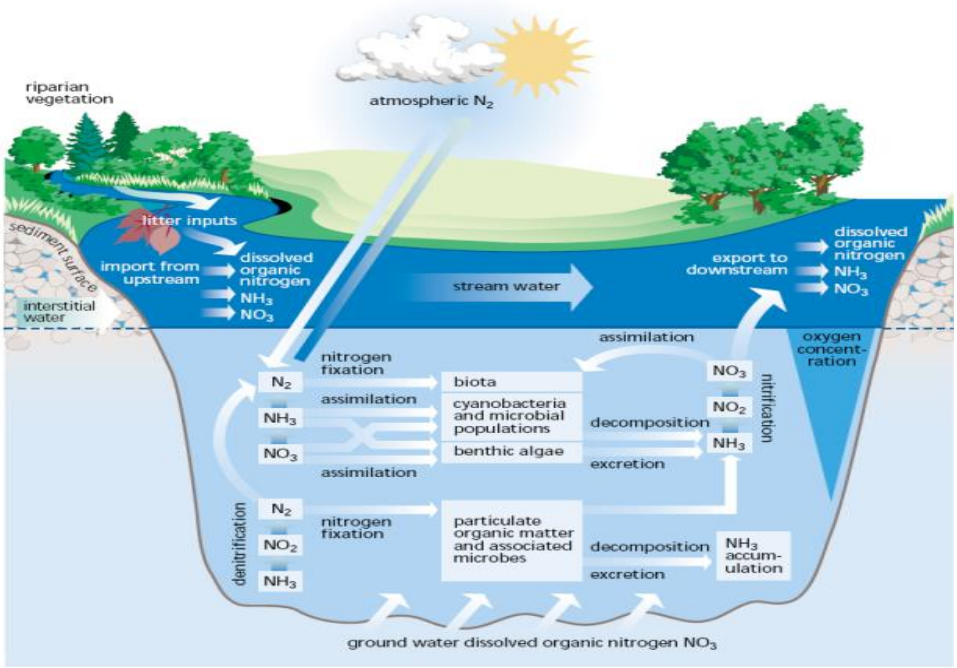


Figure 2-2: Dynamics and transformations of nitrogen in a stream ecosystem. Nutrient cycling from one form to another occurs with changes in nutrient inputs, as well as temperature and oxygen available (FISRWG, 1998).

The nitrification process converts ammonia (or ammonium) to nitrite (Eq. 1) and the nitrite to nitrate (Eq. 2). Nitrification occurs aerobically and it is carried out by microorganisms. This is a very oxygen demanding process and it occurs in a zone with high oxygen concentration (Ahn, 2006).

$$NH_4^+ + O_2 \rightarrow NO_2^- + 2H^+ + H_2O \quad \text{(Eq. 1)}$$

$$NO_2^- + O_2 \rightarrow NO_3^- \quad \text{(Eq. 2)}$$

When there is not enough oxygen, ammonia can accumulate in the water, sediments and soil (Figure 2-2).

The denitrification process converts nitrate to nitrogen gas (Eq. 3). It is desirable that the nitrogen is completely removed from the aquatic system, because nitrate accumulates and decreases the pH and/or infiltrates in the soil and contaminates ground water (Dalton & Brand-Hardy, 2003). The reaction is carried out by bacteria and is controlled by the availability of carbon, pH, temperature and residence times (Knowles, 1982).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_{2\,(g)} \quad \text{(Eq. 3)}$$

Another denitrification process called anammox (Anaerobic ammonium oxidation), a recently discovered process, can oxidize ammonium and nitrite to nitrogen gas (Eq. 4) (Strous et al., 1999).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \quad \text{(Eq. 4)}$$

Typical dynamics of nitrogen compounds in water, over time and/or downstream from a source of organic nitrogen contamination, is the result of the processes previously described (Figure 2-3).

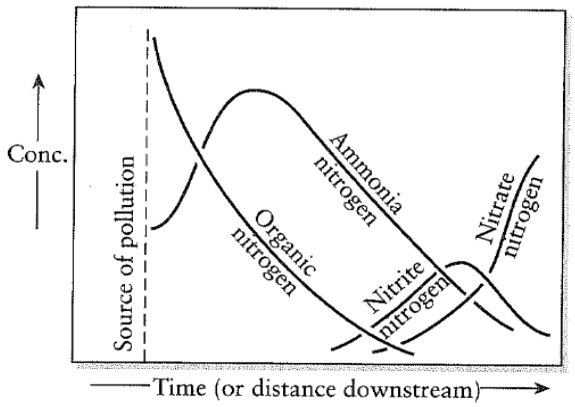


Figure 2-3: Nitrogen composition downstream from a source of organic nitrogen pollution (Vesilind & Morgan, 2004).

Unlike nitrification, denitrification is an anaerobic process, occurring mostly in soils and sediments and anoxic zones in lakes and oceans. Similar to nitrogen fixation, denitrification is carried out by a diverse group of prokaryotes, and there is recent evidence that some eukaryotes are also capable of denitrification (Trimmer et al., 2006).

Denitrification is important in that it removes fixed nitrogen from the ecosystem and returns it back to the atmosphere in a biologically inert form (N_2). In wastewater treatment, stormwater treatment and wetlands it plays a very beneficial role by removing unwanted nitrates from the wastewater effluent, thereby reducing the chances that the water discharged from the treatment plants will cause undesirable consequences (e.g. algal blooms).

In the last century, land use in urban areas has changed, increasing impervious cover, reducing vegetation, increasing channelization of streams, and resulting in the degradation of wetlands and riparian zones (Brush, 2009). This situation has reduced the urban watershed nitrogen retention functions, particularly during storm events (Kaushal et al., 2008). The change in land use has reduced the contact area of reactive nitrogen with plants and soil microorganisms, a situation that postpones and lowers the denitrification and nitrogen assimilation processes and leads to an increase of reactive nitrogen reaching the rivers, lakes and oceans.

The increase of reactive nitrogen in the nitrogen cycle becomes an issue because the nitrogen is not removed by the denitrification process or by plant and microorganisms assimilation. In high concentrations, many of the reactive nitrogen compounds are harmful and can have adverse ecological effects in the atmosphere, and in terrestrial and aquatic ecosystems (Table 2-1).

Given the intense use of fertilizers in rural areas, nitrogen compounds have been found in high concentration in rivers, groundwater and lakes. In New Zealand, the high concentration of nitrogen compounds in water bodies due to intensive dairy farming in rural areas is a known problem (Wilcock et al., 1999).

Although considerable research has been done around waterways contaminated by nitrogen compounds in rural areas, the problem also occurs in urban areas. However, limited information is available on stream nitrogen sources in urban areas.

Table 2-1: Adverse effects of nitrogen compounds in the environment (Stumm & Morgan, 1995).

Nitrogen compound	Main Origin	System Polluted	Adverse Effects
NO_3^-	Fertilizer, ammonia oxidation process	Rivers, groundwater, oceans	Health, drinking water, eutrophication
$HNO_{3(g)}$	Combustion of fossil fuels	Atmosphere, soils	Acid rain
NO_2^-	Intermediate in nitrification, denitrification and NO_3^- reduction	Waters	Toxic for fish
$NO_{(g)}$, $NO_{2(g)}$	Combustion of fossil fuels, vehicles, denitrification in soils	Atmosphere	Assists in production of ozone in troposphere, toxic effects on plants
$N_2O_{(g)}$	Intermediate in nitrification and NO3- reduction	Atmosphere	Destruction of O_3 (Ozone) in stratosphere
$NH_{3(g)}$, NH_4^+	Fertilizer, animal feed lots	Atmosphere, soil	Nitrification of NH_4^+ (from precipitates) leads to acidification of soils
		Waters	Toxicity of NH_3 to fish, increased chlorine demand in chlorination of drinking water

Ammonia is one of the most toxic form of nitrogen in water. The toxic concentration of ammonia is proportional to the pH, the higher the pH, the lower the toxic ammonia levels in water (Figure 2-4). In water, ammonia ($NH_{3\,(g)}$) is in equilibrium with ammonium ($NH_4^{+}{}_{(aq)}$; Eq. 5). Because ammonia and ammonium coexist in water, analysis results represent the sum of ammonia and ammonium as ammonia N or ammoniacal nitrogen (NH_4-N). With the increase of the pH (more hydroxide in water), the equilibrium shifts to the left, increasing the concentration of $NH_{3(g)}$, which is a gas and it is very toxic to aquatic life (Canterbury Regional Council, 2011).

$$NH_{3(g)} + H_2O \leftrightarrows NH_4^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \qquad \text{(Eq.5)}$$

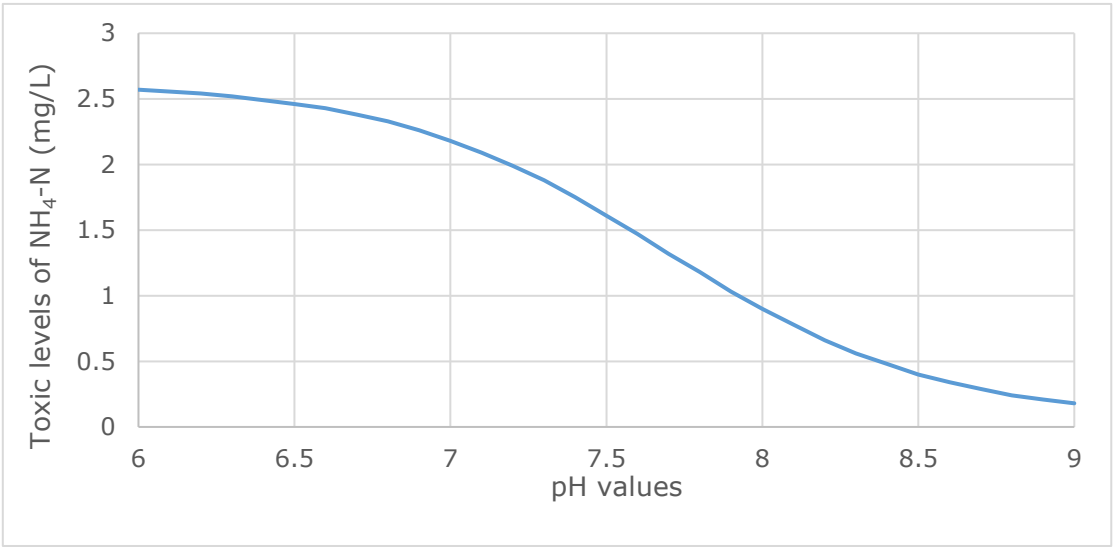


Figure 2-4: Maximum NH_4-N concentration for 95% species protection accord to Canterbury Natural Resources Regional Plan (Canterbury Regional Council, 2011).

2.2 Nitrogen in urban areas

In urban areas, the primary nitrogen inputs are food (for humans and their pets) and lawn fertilizer, although a large amount of reactive nitrogen is fixed from the atmosphere within internal-combustion chambers of automobiles (Collins et al., 2010; Elliott et al., 2007).

Land activities such as wetland conversion, impervious surfaces, and land or waterways developments, also increase or change nitrogen compounds in urban areas (Carpenter et al., 1998). Deciduous trees in urban areas lose their leaves during winter time and these are carried away into waterways by stormwater runoff, also leading to an increase of the organic nitrogen. Additionally, the biological processes in stormwater sumps, in soils in urban riparian zones and in drought ponds along streams contribute to an increase of reactive nitrogen (Collins et al., 2010; Groffman et al., 2002; Memon & Butler, 2002).

Some urban streams around the world have been reported to have high levels of nitrogen compounds. For example, a study from 2012 (Perrie, 2012) showed that all studied sites in urban areas of Wellington, New Zealand, had levels of nitrate-nitrite nitrogen higher than 0.444 mg/L, the trigger value concentration from the Australia and New Zealand Water Quality Guidelines (ANZECC, 2000). The highest value of ammoniacal nitrogen found (0.5 mg/L) was higher than the trigger ANZECC value (0.021 mg/L) and most of the urban sites had concentrations of total nitrogen (TN) higher than the trigger value of 0.614 mg/L (ANZECC, 2000). It should be noted that when ANZECC (2000) trigger values are exceeded by median water quality values at monitoring sites, then that situation should "trigger" a management response.

In New Zealand there are different guidelines for freshwater management, including national, regional and local. These include the ANZECC (2000) trigger values, the national bottom lines adopted in the National Policy Statement for Freshwater Management 2014 (Ministry for the Environment, 2014) and Canterbury Land and Water Regional Plan (Canterbury Regional Council, 2015), which are based on ecological toxicity threshold concentrations (Table 2-2).

A study performed in 2010 in the streams and rivers of Auckland, New Zealand, found that most of the urban area streams had concentrations of reactive nitrogen compounds higher than the recommended value, in particular NO_X-N (oxidized nitrogen) with 8 from 9 sites had concentrations higher than 0.444 mg/L and all the urban sites had TN concentration higher than 0.614 mg/L (Auckland City Council, 2012).

A study that used 10 years' data from the National Stormwater Quality Database in the United States from a mainly industrial land use area found median concentrations of ammoniacal nitrogen of 0.42 mg/L, oxidized nitrogen of 0.69 mg/L and total nitrogen of 2.1 mg/L (Collins et al., 2010).

Table 2-2: Guidelines for reactive nitrogen compounds (ANZECC, 2000; Canterbury Regional Council, 2015; Ministry for the Environment, 2014).

Standard Reference / Substance (mg/L)	ANZECC Trigger value for lowland river	Canterbury Land and Water Regional Plan	NPS-FM 2014 - National bottom line for toxicity	
			Annual Median	Annual 95th Percentile
Nitrate (NO_3^-)	N/A	DIN shall be less than 1.5 mg/L	6.9	9.8
NO_2^- + NO_3^-	0.444		N/A	N/A
Ammonia	0.021		1.30	2.20
Total Kjeldahl Nitrogen TKN	0.17	N/A	N/A	N/A
Total Nitrogen (TN)	0.614	N/A	N/A	N/A

In Sao Paulo city, Brazil, stormwater and part of the wastewater go straight in the local river without any treatment. The contamination by reactive nitrogen in one of its main rivers, Pinheiros River, has reached an ammoniacal nitrogen concentration of 24.2 mg/L. As a point of information, to improve the river's water quality, studies have been developed to treat the river before it leaves the city (de Barros et al., 2009).

A study conducted in Melbourne, Australia, compared the concentration of nitrogen compounds in baseflow and storm events with international literature. The mean value of 2.15 mg/L in total nitrogen was similar in both baseflow and stormflow conditions (Taylor et al., 2005). In most of the studies available, the water analyses had focused only on ammoniacal nitrogen and/or oxidized nitrogen. Since nitrogen compounds change form and are related to each other, it is important that analyses of all forms of nitrogen in water are made to help understanding the sources of the contamination and to find the best water management practices to treat the problem.

2.3 Haytons Stream

2.3.1 Haytons Stream catchment

Haytons Stream drains the southern part of the Haytons-Paparua catchment. It emerges from a reticulated stormwater network in an industrial area, located centrally within the catchment as a whole (Figure 2-5). The stream runs through an open channel for a distance of around 600 m before re-entering the pipe network for a similar distance. Around 100 m above Pilkington Way it becomes an open stream in an area of industrial and developing commercial land use and then merges with Paparua Stream. Downstream of the confluence with Paparua it enters grazing land prior to entering the Wigram Retention Basin (WRB). The outlet from the retention basin discharges almost directly into the main Heathcote/Opawaho River (Moores et al., 2009).

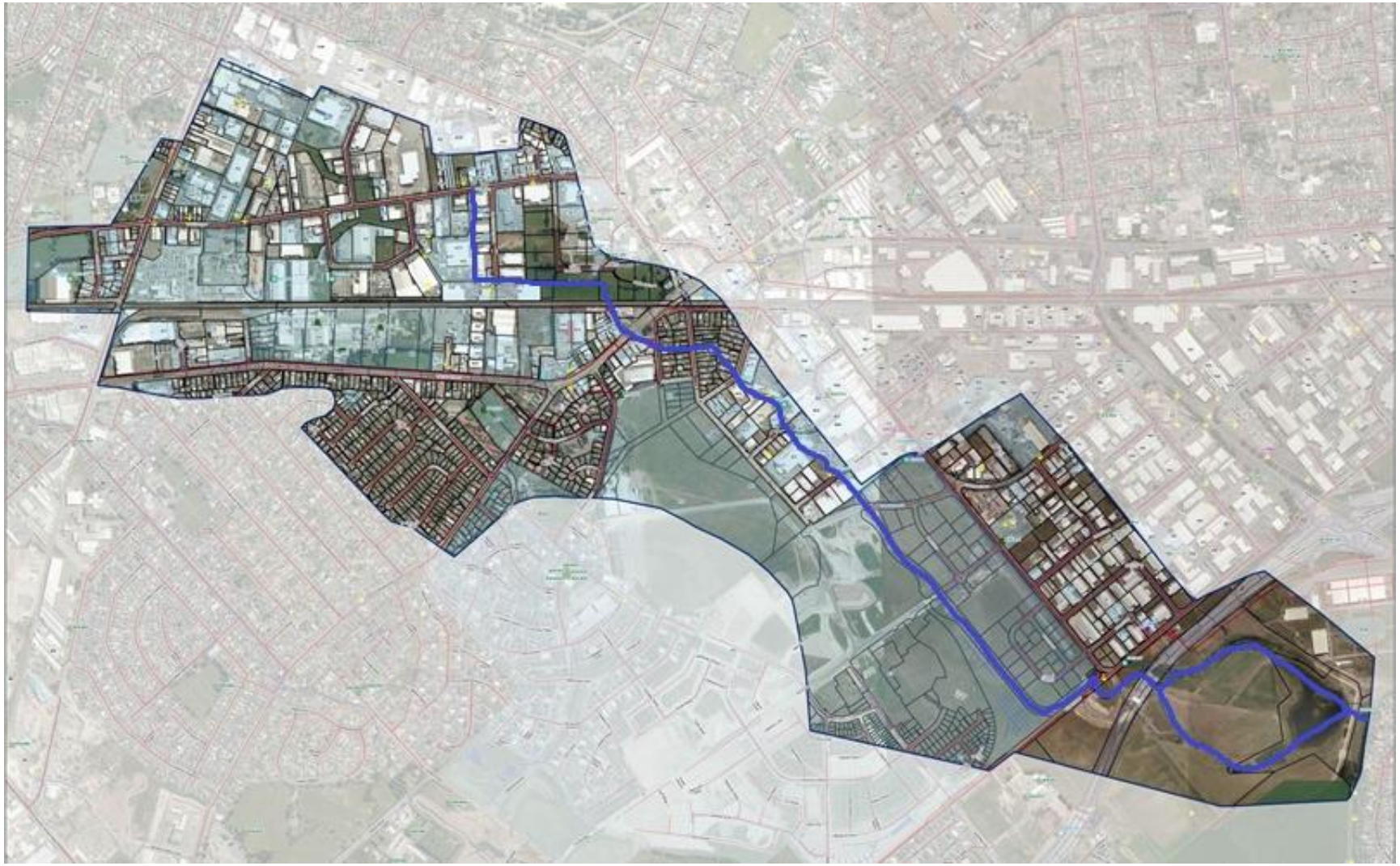


Figure 2-5: Haytons Stream catchment showing the catchment boundary and Haytons Stream waterway (dark blue).

2.3.2 Haytons Stream water quality

Environment Canterbury (ECan) has statutory responsibility under the Resource Management Act and the Local Government Act to work with the people of Canterbury to achieve sustainable management of the region's air, water and land resources. Ecan has undertaken investigations into the poor water quality of Haytons Stream in recent years due to concerns about its impact on the Heathcote River downstream, with reactive nitrogen compounds being one of the main contaminants of concern.

From 1992 to 2006, concentrations of oxidized nitrogen were monitored by ECan in the Haytons Stream upstream and downstream the Wigram Retention Basin. The reported median concentrations were 0.43 mg/L of oxidized nitrogen (n=55) and 0.76 mg/L of ammoniacal nitrogen (n=56) for the upstream site and 0.43 mg/L of oxidized nitrogen (n=65) and 0.85 mg/L of ammoniacal nitrogen (n=68) for the downstream site (ECan, 2007). The concentrations of oxidized nitrogen were close to the ANZECC trigger value (0.444 mg/L) but lower than the NPS-FM toxicity levels. Although the ammoniacal nitrogen concentrations up and downstream were high, it was lower than the annual median value of 1.3 mg/L, the national bottom line for toxicity levels for 80% of species protection (ANZECC, 2000; Ministry for the Environment, 2014).

Although a higher concentration of oxidized nitrogen after the wetland is expected, due to the nitrification processes that occurs there, a higher concentration of ammoniacal nitrogen is uncommon. The two sites had the highest concentrations of ammoniacal nitrogen that were reported in the technical analysis of long-term data up to 2006, which also included sites throughout the catchments of the rivers Avon/Otakaro and Heathcote/Opawaho in Christchurch (ECan, 2007).

In 2009, an investigation conducted in five sites at Haytons Stream were monitored in dry and wet weather using first manual sampling and then automatic samplers (Moores et al., 2009). The first site, identified as HAS-GCP, was at Gerald Connolly Place where Haytons becomes an open stream, crossing a dense industrial area. The second site, identified as HAS-SYR, was located in Symes Road and is a piped tributary of Haytons Stream in an industrial area. Downstream of those sites, at Haytons Road, where Haytons merges with Paparua Stream, was the third site, identified as HAS-HTR. The last

two sites, were in the same locations as the previous monitoring sites, one upstream of the Wigram Retention Basin (HAS-UWB) and one downstream (HAS-DWB).

Although the concentration of ammoniacal nitrogen at HAS-UWB and HAS-DWB was found to be higher than guideline values, it was lower than the concentrations reported from 1992 to 2006. The concentration of oxidized nitrogen was higher than the previous study, which suggests that the ammonia had been converted to nitrate/nitrite due to the nitrification process.

Abnormally high levels of ammoniacal nitrogen were also noted in the stream (100 mg/L on 22/07/2009 and 54 mg/L on 24/07/2009 at HAS-HTR; 57 mg/L at the HAS-SYR on 22/07/2009; 33 mg/L on 20/03/2009, 39 mg/L on 04/07/209 and 24 mg/L on 22/07/2009 at HAS-GCP)(Moores et al., 2009). This suggests discharges to Haytons Stream. Because this study did not measure the composition of all forms of nitrogen, it was not possible to quantify or understand the nitrogen composition along the stream. In addition, the low stream flow and some dry points along the stream do not contribute to a good interpretation of these data.

Given the high nitrogen concentration values found at the Gerald Connolly Place site (HAS-GCP) in 3 events, and ongoing pollution prevention work by ECan, a follow up investigation was undertaken at the HAS-GCP site in 2013 in order to check if any improvements in water quality could be detected (O'Sullivan & Charters, 2014). The study found median values of oxidized nitrogen of 0.5 mg/L under baseflow and 0.65 mg/L under stormflow conditions, which is higher than the trigger level of 0.444 mg/L. The concentration of NH_4-N was found to be around 1.7 mg/L under baseflow and 3.5 mg/L under stormflow conditions. Both values were very high and above the national bottom line for ammonia toxicity which has an annual median threshold concentration of 1.3 mg/L (ANZECC, 2000; Ministry for the Environment, 2014).

Most of the nitrogen analyses in urban stream focus only on the oxidized nitrogen and ammoniacal nitrogen, leaving aside the organic nitrogen. Depending on the nature of the catchment, type of pollutants and presence of human activities, organic nitrogen can represent a relatively big proportion of the nitrogen compounds in water.

It is still not clear where this nitrogen along Haytons Stream is coming from, whether it is a regular or a random event, or whether it originates from organic or oxidized nitrogen. As such, there is a need for a better understanding of the principal sources and compounds of nitrogen contamination in this urban stream, and the transport and fate of nitrogen compounds along and their interaction with the stream.

Understanding the dynamics of nitrogen composition in urban runoff help identify an appropriate pollutant treatment system. Once the concentrations and dynamics of each nitrogen compound is known for each flow condition and season, better stormwater management practices can be achieved.

As well as informing management options to reduce the nitrogen contamination issues in Haytons Stream, the knowledge gained should be applicable to other similar streams with industrial and commercial land use in their catchments.

2.4 Aim and objectives

The aim of this research is to characterize the nitrogen compounds in the Haytons Stream to have a better understanding of their sources and to identify stormwater management practices to deal with these type of pollutants.

The main objectives of this research are to:

1. Fully characterize composition of nitrogen compounds along Haytons Stream;
2. Understand how nitrogen compounds change with flow conditions and season along the stream;
3. Identify potential factors that affect the dynamics of nitrogen compounds in Haytons Stream (such as discharges, riparian zone, land use, wetland processes, or other factors).

3 Methodology

In order to achieve the first objective, nitrogen compounds were characterized in terms of: particulate organic nitrogen (for particles greater than 0.45 nm) (PON), dissolved organic nitrogen (DON), ammoniacal nitrogen (NH_4-N) and oxidized nitrogen (NO_X-N). In order to determinate each concentration, water samples were analyzed for total nitrogen (TN), total dissolved nitrogen (TDN), ammoniacal nitrogen (NH_4-N) and oxidized nitrogen (NO_X-N). PON concentration was estimated from the difference between TN and TDN, whereas DON was calculated from the difference between TDN and [(NO_X-N) + (NH_4-N)] (Taylor et al., 2005).

To achieve the second objective, different sampling sites along Haytons Stream were sampled under baseflow and stormflow conditions during the dry and the wet seasons.

To achieve the third objective, the trend of change of nitrogen compounds along the stream and with weather condition was compared to that of dissolved oxygen, pH, turbidity, conductivity and temperature. In addition, street runoff and stream bed sediments were also analyzed to better understand the dynamic of nitrogen compounds in Haytons Stream.

3.1 Sampling sites

Haytons Stream is approximately 4.3 kilometres long. Eight sampling sites (Figure 3-1) were selected along its length at locations where sampling was done in previous studies and considering other factors such as where changes of the stream's course occurred, accessibility, runoff from different land uses, and locations where water flows during the whole year.

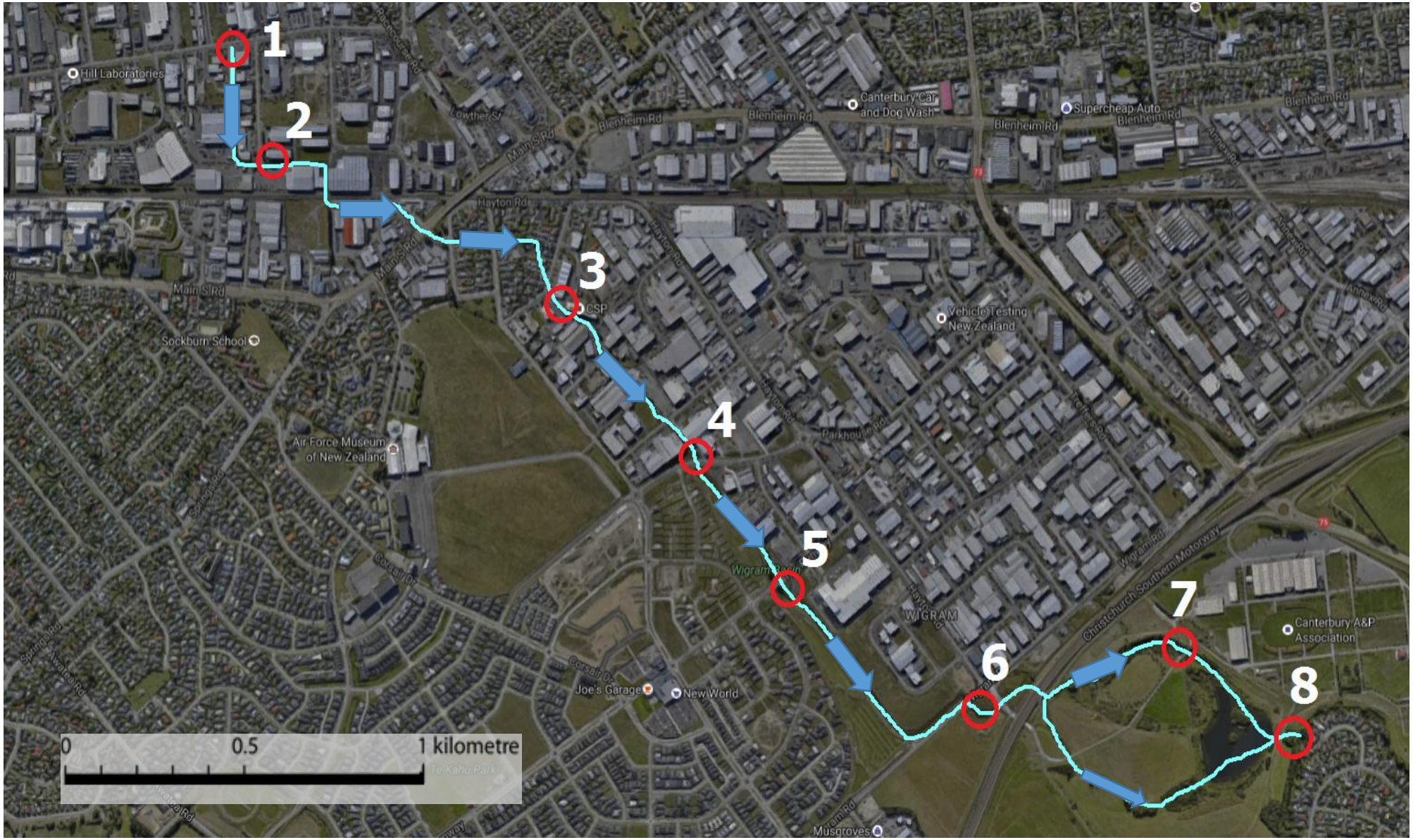


Figure 3-1: Sampling sites (red circles) along Haytons Stream (green line) and blue arrows showing the water flow (background aerial image from maps.google.co.nz).

Site 1: This site is located at Waterloo Road (43°32'14.9"S, 172°32'30.3"E) where Haytons Stream first becomes an open stream. This sampling site was chosen because of its accessibility and because there is water to be sampled, even in dry weather, due to the existence of a pond. To accomplish the objectives of understanding the dynamics of nitrogen compounds, this site is ideal because it is the most upstream site (Figure 3-2).

Figure 3-2: Site 1 during one of the sampling campaigns. Often rubbish was found around the site.

Site 2: This site is located at Gerald Connolly Place (43°32'24.9"S, 172°32'35.0"E), around 400 meters downstream from Site 1. In 2013, NH_4-N and NO_x-N concentration during stormflow and baseflow events were measured and compared at this site (O'Sullivan & Charters, 2014). This site was chosen because the availability of previous data, because it has easy access, and because 150 meters downstream Haytons Stream becomes a piped stream (Figure 3-3).

Figure 3-3: Site 2 during a sampling campaign under baseflow conditions.

Site 3: This site is located in an industrial area at Washbournes Road (43°32'36.6"S, 172°33'11.8"E), around 900 meters downstream of Site 2. This site was selected because between Sites 2 and this location, Haytons Stream merges with a tributary from the southwest part of the catchment as well as Haytons' becomes an open stream permanently at this point. This sampling location is easily accessible but occasionally gets dry and there is almost no water to be sampled (Figure 3-4).

Figure 3-4: Sampling Site 3 under baseflow conditions.

Site 4: This site is located at Lodestar Avenue (43°32'49.9"S, 172°33'30.0"E), around 600 meters downstream of Site 3. At this location, Paparua and Haytons Streams merge. This site has a history of high NH_4-N concentration. In addition, Haytons Stream's course was changed downstream of this site and the riparian zone was restored and improved. This site has an easy access and presence of water the whole year. The sampling point is upstream of the bridge, where is can be easily accessed (Figure 3-5).

Figure 3-5: Drone picture showing Haytons Stream waterways flowing between two white buildings merging Paparua Stream, which comes from a white pipe directly upstream of the pond.

Site 5: This site is located at The Runway (43°33'01.0"S, 172°33'41.0"E), 450 meters downstream of Site 4. This site is part of the new course of Haytons Stream, which flows along a developing urban, commercial and industrial area. The sampling point is situated downstream of the bridge where a wet pond is located, with an easy access and presence of water during the whole year (Figure 3-6).

Figure 3-6: Drone picture of Haytons Stream waterways showing Site 4 at the top, the developing land use surrounding the stream and Site 5 downstream the bridge.

Site 6: This site is located south of Wigram Road (43°33'11.5"S, 172°34'07.5"E), 800 meters downstream of Site 5. This site is where Haytons Stream enters into the Canterbury Agricultural Park. It is situated in a wet pond with easy access and presence of water during the whole year (Figure 3-7).

Figure 3-7: Drone picture of Site 6, showing Wigram Road on the top right and the sampling point on the bottom left of the picture, output of the pond.

Site 7: This site is located in the Canterbury Agricultural Park (43°33'06.7"S, 172°34'32.0"E), 650 meters downstream of Site 6. This site is just upstream of Wigram Retention Basin, a wetland located at the very end of Haytons Stream Catchment. This site was chosen because high levels of nitrogen compounds were previously monitored at this site. This site is essential to understand the dynamics of nitrogen compounds before and after the wetland (Figure 3-8 and 3-10).

Figure 3-8: Drone picture showing Site 7, upstream of the bridge, surrounded by a riparian zone.

Site 8: This site is located at the output of Wigram Retention Basin (43°33'13.9"S, 172°34'45.6"E), 30 meters upstream from where Haytons Stream merges with Heathcote River. Previous studies showed levels of nitrogen compounds higher than local guidelines (Moores et al., 2009). This site is also essential to understand the dynamics of nitrogen compounds in the wet pond and its discharge into the Heathcote River (Figure 3-9).

Figure 3-9: Sampling point of Site 8, downstream the Wigram Retention Basin.

Figure 3-10: Wigram Retention Basin downstream Site 7 and upstream Site 8.

3.2 Sampling campaigns

At the start of this project, only Sites 2, 4, 7, and 8 were sampled during baseflow and stormflow conditions. The results of those four sites indicated that the concentration of nutrients and water quality did change along the stream. The number of sites sampled on each campaign was thus increased to have a better overview of the nitrogen compounds along Haytons Stream. As a result, some sites were sampled only once during the dry season.

3.2.1 Dry season

During the dry season (summer in New Zealand) four baseflow and five stormflow sampling campaigns were performed from 9/9/2015 to 13/04/2016. All the selected sites were sampled during the dry season campaign and the four main sites (Sites 2, 4, 7 and 8) were sampled 3 times or more (Table 3-1).

Table 3-1: Sampling dates and flow conditions of each sampled site during the dry season sampling campaign.

Date	Conditions	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
9/09/2015	Baseflow	x	x		x			x	x
28/10/2015	Stormflow	x	x		x			x	
3/02/2016	Baseflow		x	x	x			x	x
17/02/2016	Stormflow	x	x	x	x		x	x	x
1/03/2016	Baseflow	x	x		x			x	x
15/03/2016	Stormflow	x	x	x	x		x	x	x
24/03/2016	Stormflow	x	x	x	x	x	x	x	x
31/03/2016	Baseflow	x	x	x	x	x	x	x	x
Total Baseflow Water Samples		n=4	n=5	n=2	n=5	n=1	n=1	n=4	n=4
Total Stormflow Water Samples		n=4	n=4	n=3	n=4	n=1	n=3	n=4	n=3

3.2.2 Wet season

The Wet Season occurs during the wintertime in New Zealand and samples were taken from 07/06/2016 to 13/07/2016 under baseflow and stormflow conditions (Table 3-2). This sampling campaign was shorter than the one during the dry season because of more frequent rain events. All eight sites were sampled on each sampling campaign, alternating samplings under baseflow and stormflow conditions.

Table 3-2: Sampling dates and flow conditions of each sampled site during the wet season sampling campaign.

Date	Conditions	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
07/06/2016	Baseflow	x	x	x	x	x	x	x	x
23/06/2016	Stormflow	x	x	x	x	x	x	x	x
29/06/2016	Baseflow	x	x	x	x	x	x	x	x
8/7/2016	Stormflow	x	x	x	x	x	x	x	x
11/07/2016	Baseflow	x	x	x	x	x	x	x	x
13/7/2016	Stormflow	x	x	x	x	x	x	x	x
Total Baseflow Water Samples		n=3	n=3	n=3	n=3	n=3	n=3	n=3	n=3
Total Stormflow Water Samples		n=3	n=3	n=3	n=3	n=3	n=3	n=3	n=3

3.3 Water analysis

Water samples were manually collected in 1-L PET bottles (Figure 3-11), stored in a cooler containing ice and immediately transported to UC's Environmental Engineering Laboratory for analysis. Only water temperature and dissolved oxygen were measured on site with field equipment. Samples were stored in a refrigerator at 4°C after their pH was adjusted to below 2 with concentrated sulfuric acid for preservation. Before analysis, the samples' pH was neutralized. Information of sample size, storage requirements before preservation are described as well as laboratory analysis, units, range and equipment used on this study (Table 3-3; Table 3-4). The following sections describe in details the analysis methods performed in this study

Figure 3-11: Sampling bottles containing Haytons Stream water collected on 03/02/2016, showing samples from Sites 2, 3, 4, 7 and 8 (from left to right).

Table 3-3: Summary of sample preservation and storage requirements before preservation.

Analytical parameter	Container	Minimum sample size (mL)	Preservation	Maximum storage time
TN (Total Nitrogen)	Plastic	50	Refrigerate	24 hours
NO_X-N (Oxidized Nitrogen)	Plastic	50	Refrigerate	24 hours
NH_4-N (Ammoniacal Nitrogen)	Plastic	125	Refrigerate	24 hours
DO (Dissolved Oxygen)	Must be done in the field			
pH	Plastic	125	Refrigerate	6 hours
Turbidity	Plastic	125	Refrigerate	24 hours

Plastic = polyethylene or equivalent
Refrigerate = storage at 1-4°C in the dark
Source: Department of Water, Australia, www.water.wa.gov.au

Table 3-4: Parameters and equipment used on each water analysis.

Analysis	Units	Range	Instrument
pH	-log[H+]	0-14	EDT RE 357 Tx pHmeter
Dissolved oxygen	%	0-500	YSI 550A Dissolved Oxygen
Conductivity	µS/cm	0-20000	YSI 30-10 FT Conductivity meter
Turbidity	NTU	0-1000	HACH 2100P Turbidimeter
Temperature	°C	-5 to 45	YSI 550A Dissolved Oxygen
TN and TDN	mg N/L	0.5-25.0	HACH DRB 200 Digester and HACH DR 3900 Spectrophotometer
NO_X-N	mg N/L	0.1-10.0	HACH DR 3900 Spectrophotometer
NH_4-N	mg N/L	0.1-0.6	Thermo Scientific Genesys 10S UV-Vis Spectrophotometer

3.3.1 Total nitrogen

Total Nitrogen (TN) was analyzed using HACH's Method 10071 (HACH, 2003). This method consists of three steps. The first step was mixing reagent A with the sample solution and then digesting at 105°C for 30 minutes. Once the solution had cooled down to room temperature, Reagent B was mixed with the solution for 15 seconds and the resulting solution reacted for 2 minutes (step 2). For the last step, 1 mL of the solution was added into a solution B, slowly mixed, reacted for 5 minutes and then the absorbance was read at 410 nm. A blank solution with deionized water was also prepared following the same procedure.

As recommended by the method, a 10 mg/L standard solution was tested to verify the accuracy of the test. An improved accuracy was reached by increasing the shaking and reaction time by 10%. This was verified against a standard solution containing 5 mg/L of TN. Before analysis, the sample pH was neutralized with concentrated sulphuric acid or sodium hydroxide. In addition, a quality control solution together with a duplicate of one of the samples were used during the analysis to verify accuracy.

3.3.2 Total dissolved nitrogen

Total Dissolved Nitrogen (TDN) was analyzed by filtering the sample using a 0.45 µm membrane and then following the same procedure as for TN analysis.

3.3.3 Ammoniacal nitrogen

Ammoniacal nitrogen (NH_4-N) was measured using the Phenate Standard Method (4500-NH3 F) (APHA, 1999). This method consists of reacting 25 mL of sample, 1 mL of 10% phenol in ethyl alcohol solution, 1 mL of 0.5% (w/v) sodium nitroprusside in water and 2.5 mL of an oxidizing solution (mix of 5% bleach and alkaline citrate solution). This method is linear up to 0.6 mg/L of NH_4-N. When concentrations were above 0.6 mg/L, dilution was necessary to obtain an accurate result. Samples were diluted up to 10 times. If the sample was still below the maximum concentration for the analysis then HACH Method 10031 was used (HACH, 2003). Before the analysis, the sample was filtered using a 0.45 µm membrane to minimize or avoid interference during the analysis.

A standard curve was prepared using standard solutions with concentrations of 0.0, 0.1, 0.2, 0.4 and 0.6 mg/L of NH_4-N. A quality control (QC) solution was used to verify the accuracy of the test along with one duplicate sample to verify the test performance (Figure 3-12).

Figure 3-12: Solutions containing concentrations of 0.0, 0.1, 0.2, 0.4 (duplicate) and 0.6 mg/L of NH_4-N and the reagents solutions of phenol and sodium nitroprusside used to calculate the standard curve.

3.3.4 Oxidized nitrogen

Oxidized Nitrogen (NO_X-N) was measured using HACH's Nitrate Method 8039 (HACH, 2003). This method consists of mixing a HACH reagent NitraVer 5 with 10 mL of the sample, mixed for one minute and reacted for five minutes. Sample absorbance was read at 430 nm. A blank solution with deionized water was also prepared following the same procedure. A 10 mg/L standard was used to verify the test's accuracy. Before analysis, samples pH were neutralized with sulphuric acid or sodium hydroxide for more accurate results

Accuracy of detection was improved by increasing the shaking and reaction time by 10%. This process lead to better results as verified with a standard solution containing 5 mg/L of NO_X-N. A quality control solution together with a duplicate of one of the samples were used during the analyses.

3.4 Street runoff

Analyses of the street runoff before it enters the stream were made to evaluate the concentration of nitrogen compounds that goes into the stream in a storm event. Samples were collected at Site 2 so that they could be compared to previous water quality monitoring for baseflow and stormflow conditions at that site (O'Sullivan & Charters, 2014). Street runoff samples were collect on 28/10/2015, 17/02/2016 and 15/03/2016.

3.5 Stream bed sediment sampling

Sediments were taken from Haytons Stream's bed on 26/11/2015 at Sites 1, 2 and 4. Those locations were selected because of high concentrations of ammoniacal nitrogen were previously observed (ECan, 2007; Moores et al., 2009; O'Sullivan & Charters, 2014). Sediments were collected from different points on each site and mixed to ensure a representative sample. Samples were sent to an accredited Laboratory to be analyzed for NH_4-N (mg/kg of dry matter).

3.6 Laboratory-based temporal nitrogen change experiments

Laboratory-based experiments were designed to better understand the changes in nitrogen in the sediment and in the water over time. Sediment and water samples for these experiments were collected from Site 4. The following describes each experiment.

3.6.1 Stream bed sediment experiment

In this laboratory-based experiment, collected sediment samples were left outdoor in a closed container (covered bucket) for a period of a month (13/04/2016 - 11/05/2016; Figure 3-13). Weekly samples were taken to evaluate the changes on NH_4-N concentration over time. This experiment could be associated with the processes than happens in the riverbeds and inside stormwater pipe system, which contains sediments, organic matter and water.

To extract the nutrients for laboratory quantification, 4 grams of sediment and 40 mL of fresh deionized water were added in four different centrifuge tubes. The tubes were mixed for 4 hours at 30 rpm. Subsequently, the tubes containing the mix were centrifuged for 10 minutes at 4100 rpm. Samples were then filtered using a 0.45 micron filter. Once the nutrients were extracted, analyses of TDN, NO_X-N, NH_4-N and pH were performed. A test to determinate the dry matter was also performed on each sample, because of elevated percentage of water on it. The results were expressed in mg/kg of dry matter.

Figure 3-13: Closed container (bucket) containing stream bed sediment.

3.6.2 Water column incubation experiment

A water column incubation experiment was conducted to verify the nitrogen dynamics in water over time. Water with elevated concentration of nitrogen compounds and stream bed sediment sample from Haytons Stream at Site 4 were stored in two transparent containers and left outdoors for a period of a month (31/03/2016–28/04/2016). Column A had more sun exposure than column B (Figure 3-14). Weekly samples were taken and analysed in terms of TN, TDN, NO_X-N, NH_4-N and pH to verify the changes over time.

3.7 Statistical analysis

A t-test was used to verify the significance of the difference in nitrogen compounds concentration along Haytons Stream for different flow condition, seasons and sites. Due to the different numbers of samples taken on each site as well as at different flow conditions and seasons, the unequal variances t-test was used. The assumption was that the differences were significant at p=0.10.

Figure 3-14: Water column incubation experiment with experiment A on the left side and experiment B on the right side.

4 Results

This section describes results from the laboratory analysis and in-situ measurements at the eight sites located within Haytons Stream catchment for the sampling campaigns conducted during the dry season and the wet season. Seasonal differences and flow conditions (baseflow versus stormflow) are compared for all sites along Haytons Stream.

4.1 Total nitrogen

Total Nitrogen (TN) concentrations showed a similar trend of variation during the wet and dry seasons, with concentrations increasing from the upper part of the stream to the middle and decreasing from the middle part to the lower part of the stream. There was no significant difference in TN concentration between Sites 1 and 2 (Figure 4-1; Table 4-1).

The highest increase in TN found at Haytons Stream occurred between Sites 2 and 3 where the mean concentration of TN was found to increase from 3.1 mg/L to 10.2 mg/L (Table 4-1). A peak concentration of 46.8 mg/L occurred during the dry season at Site 3 where the mean TN concentration increased from 2.6 mg/L under baseflow up to 15.6 mg/L under stormflow conditions (Figure 4-1).

Between Sites 3 and 6, a decrease in TN was noticed for both baseflow and stormflow conditions, but no significant difference was found. At Site 7 an increase in TN was observed, but no significant difference from the upstream sites (Table 4-1; Figure 4-1).

Mean TN concentrations and variance decreased from the input (Site 7) to the output (Site 8) of the WRB at the lower Haytons. Although under baseflow conditions and also during the wet season this decrease was not significant, under stormflow conditions, during the wet season and overall baseflow versus stormflow conditions the difference was very significant (Table 4-1; Figure 4-1).

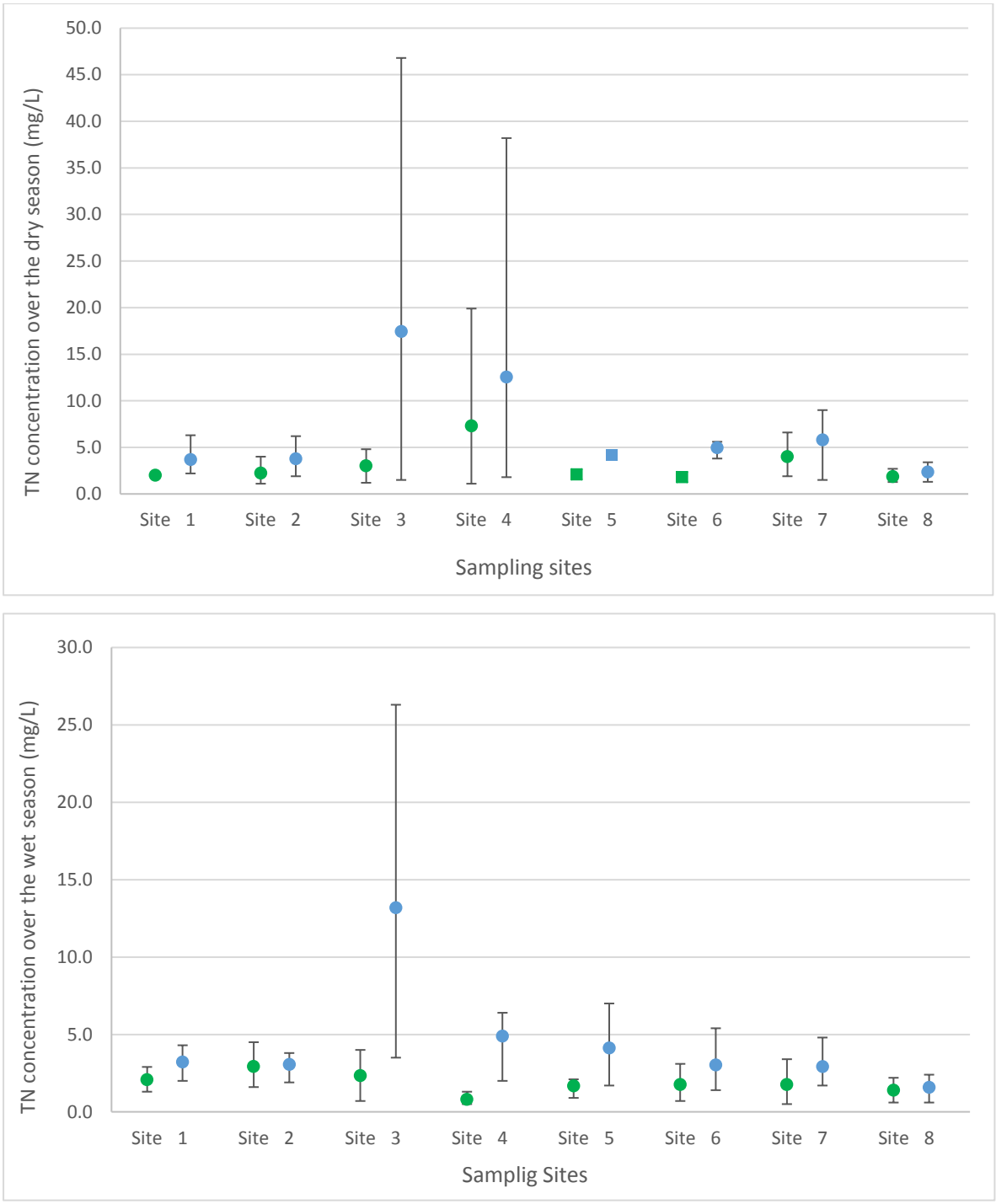


Figure 4-1: Total nitrogen concentrations along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

Table 4-1: Summary of t-test results with mean concentrations of TN between sites, flow conditions and seasons; p-values show the difference between a row and the row above; red p-values represent a very relevant difference and yellow a relevant difference.

Criteria	Site and/or condition	Number of samples	Mean TN (mg/L)	Variance	P-value
Individual Sites	Site 1	14	2.9	1.878	
	Site 2	15	3.1	2.011	0.7487
	Site 3	12	10.2	183.766	0.0963
	Site 4	15	7.3	100.822	0.5391
	Site 5	8	3.0	3.806	0.1282
	Site 6	10	3.1	3.481	0.8731
	Site 7	15	3.9	6.201	0.3514
	Site 8	14	1.8	0.675	0.0067
Flow conditions for individual sites	Site 3 - baseflow	5	2.6	3.115	
	Site 3 - stormflow	7	15.6	252.312	0.0749
	Site 7 - baseflow	7	3.0	4.283	
	Site 8 - baseflow	7	1.7	0.505	0.1371
	Site 7 - stormflow	8	4.7	7.222	
	Site 8 - stormflow	7	2.0	0.876	0.0261
	Site 1 - baseflow	6	2.0	0.271	
	Site 8 - baseflow	7	1.7	0.505	0.2920
	Site 1 - stormflow	8	3.5	2.205	
	Site 8 - stormflow	7	2.0	0.876	0.0358
Seasons for Individual sites	Site 7 - dry season	9	5.0	6.210	
	Site 8 - dry season	8	2.1	0.648	0.0079
	Site 7 - wet season	6	2.4	2.371	
	Site 8 - wet season	6	1.5	0.604	0.2666
Overall baseflow vs. stormflow conditions for different seasons	Baseflow - dry season	23	3.4	15.564	
	Stormflow - dry season	32	7.1	95.557	0.0571
	Baseflow - wet season	24	1.9	1.277	
	Stormflow - wet season	24	4.5	26.211	0.0195
Overall baseflow vs. stormflow conditions	Baseflow	47	2.6	8.674	
	Stormflow	56	6.0	66.498	0.0048
Overall dry vs. wet seasons	Dry Season	55	5.5	64.668	
	Wet Season	48	3.2	15.273	0.0566

There was a significant difference in TN concentrations between Sites 1 and 8 (upper and lower part of Haytons) under stormflow conditions, but under baseflow conditions the difference in TN concentration was not significant (Table 4-1; Figure 4-1).

Comparing flow conditions, there was a very significant difference between baseflow and stormflow conditions, being more significant during the wet season than during the dry season. In addition, the variation in TN concentrations were found to be higher during the dry season compared to the wet season, significant difference (Table 4-1).

For a better overview and understanding of the nitrogen compounds along Haytons Stream, the percentage of each nitrogen compound on each sampling site was calculated under baseflow and stormflow conditions for the dry and wet seasons (Figure 4-2).

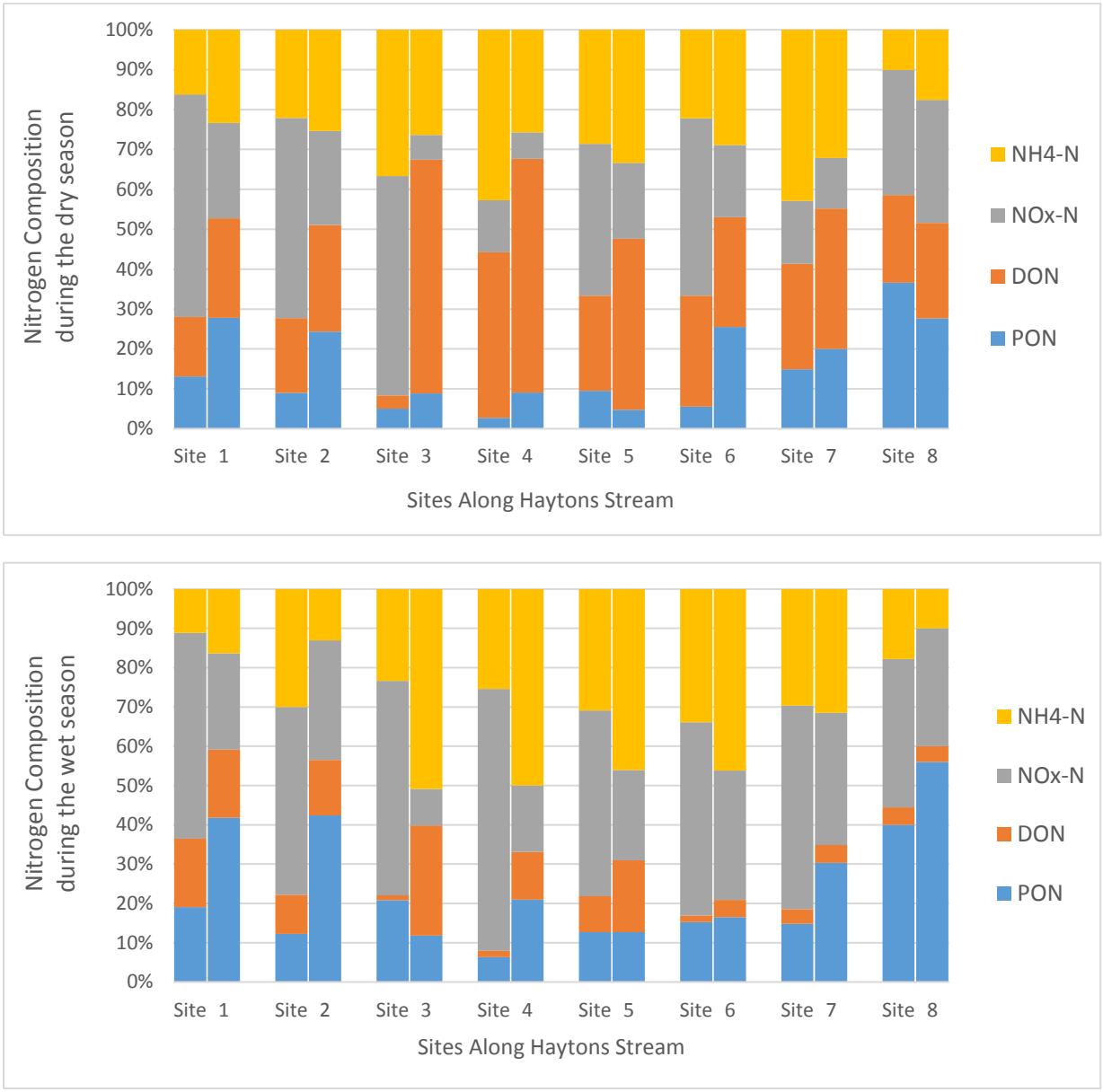


Figure 4-2: Nitrogen composition along Haytons Stream under baseflow (left bar) and stormflow (right bar) conditions during the dry (top graph) and the wet (bottom graph) seasons.

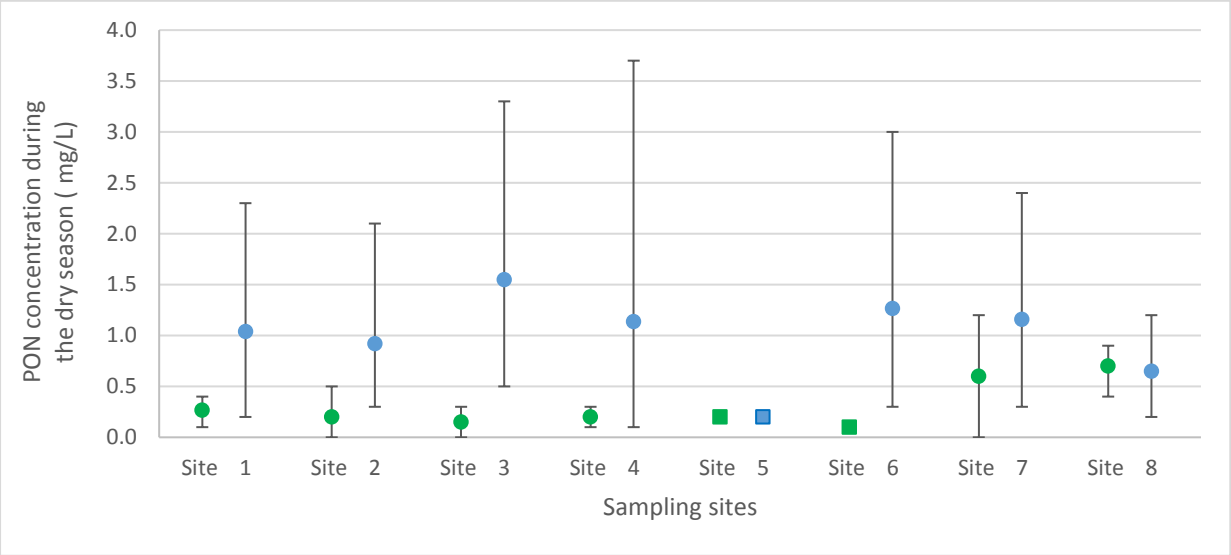
4.2 Particulate organic nitrogen

PON concentrations were found to be higher during stormflow conditions compared to baseflow conditions but mean concentrations were found to be similar in both wet and dry seasons, with the greatest variance observed during the dry season under stormflow conditions. No difference in PON concentrations were found between the dry and the wet seasons (Figure 4-3; Table 4-2).

The highest concentrations in PON were found at Sites 3 and 4 but there were no statistical differences in PON concentrations between the sites along Haytons Stream (Figure 4-3). Even though Site 8 had a mean concentration lower than other sites, PON represented around 40% of the TN during baseflow conditions and between 30% and 60% during stormflow conditions, which is a higher percentage than in any other sites along Haytons Stream (Figure 4-3).

Table 4-2: Summary of t-test results with mean concentrations of PON between sites, flow conditions and seasons; p-values shows the difference between a row and the row above; red p-values represent a very relevant difference.

Criteria	Site and/or condition	Number of samples	Mean PON (mg/L)	Variance	P-value
Overall baseflow vs. stormflow conditions for different seasons	Dry season - baseflow	23	0.4	0.124	
	Dry season - stormflow	32	1.1	0.997	6.193E-4
	Wet season - baseflow	24	0.3	0.122	
	Wet season - stormflow	24	1.0	0.395	5.411E-5
Overall baseflow vs. stormflow conditions	Baseflow	47	0.4	0.120	
	Stormflow	56	1.0	0.728	3.949E-7
Overall dry vs. wet seasons	Dry season	55	0.8	0.748	
	Wet Season	48	0.7	0.368	0.5483



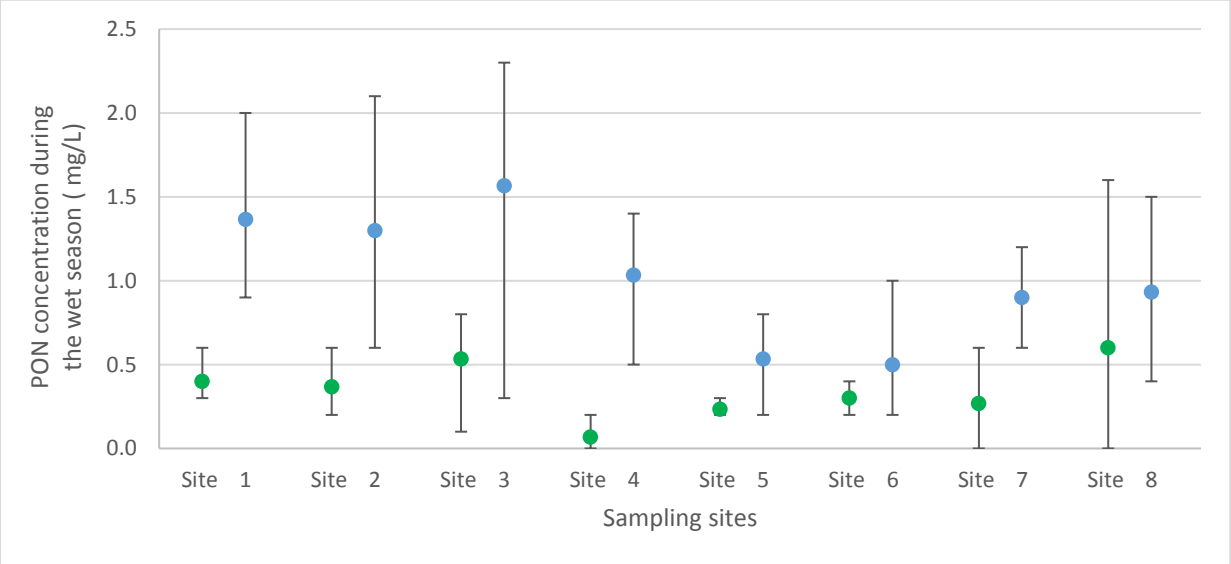


Figure 4-3: Particulate organic nitrogen concentrations along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.3 Dissolved organic nitrogen

DON concentrations were found to have a similar trend of variation compared to TN concentrations along Haytons Stream (Figure 4-4). No statistical significance was found between sampling sites, except between Sites 7 and 8 (Table 4-3).

Comparing Sites 3 and 4 with Sites 1 and 2 and also with Sites 5 and 6, a very significant difference was found: mean concentrations in DON increased from 0.6 mg/L at Sites 1 and 2 to 3.8 mg/L at Sites 3 and 4, and decreased to 0.6 mg/L at Sites 5 and 6 (Table 4-3). In addition, the five greatest peaks in DON concentration were found at Sites 3 and 4 with concentrations up to 31.1 mg/L (Table 4-4).

Regarding flow conditions, during the dry season the mean concentration and variance in DON was found to be higher in both baseflow and stormflow conditions compared to the wet season, with the difference being significant during the dry season. Overall, concentrations and variance in DON under baseflow conditions were found to be significantly much lower than under stormflow conditions (Table 4-3, Figure 4-4).

Comparing the seasons, mean concentration in DON during the dry season was more than four times higher than during the wet season, a very significant difference in mean concentration (Table 4-3).

At Sites 3 and 4 mean DON concentrations were found to be 1.0 mg/L during the wet season and 6.0 mg/L during the dry season. Large differences between seasons were also observed at Sites 7 and 8, with the lowest levels in DON concentrations found at Site 8 (Table 4-3, Figure 4-4).

The sampling campaign on 23/06/2016 found TN concentration of 26.3 mg/L at Site 3, with 10.7 mg/L of DON (Table 4-4). This water sample were sent to an accredited lab to be tested for Urea. Analysis showed 10.5 mg/L of Urea in that sample, in other words, urea represented around 98% of the DON.

Table 4-3: Summary of t-test results with mean concentrations of DON between sites, flow conditions and seasons; p-values shows the difference between a row and the row above; red p-values represent a very relevant difference and yellow a relevant difference.

Criteria	Site and/or condition	Number of samples	Mean DON (mg/L)	Variance	P-value
Individual Sites	Site 1	14	0.6	0.385	
	Site 2	15	0.6	0.359	0.9912
	Site 3	12	4.4	82.033	0.1779
	Site 4	15	3.4	46.379	0.7584
	Site 5	8	0.6	0.706	0.1445
	Site 6	10	0.5	0.419	0.7294
	Site 7	15	1.0	1.624	0.2157
	Site 8	14	0.3	0.120	0.0590
Group of sites	Sites 1 and 2	29	0.6	0.358	
	Sites 3 and 4	27	3.8	59.927	0.0404
	Sites 5 and 6	18	0.6	0.519	0.0389
Seasons for Individual sites	Sites 3 and 4 - dry season	15	6.0	92.515	
	Sites 3 and 4 - wet season	12	1.1	9.335	0.0803
	Site 7 - dry season	9	1.6	1.804	
	Site 7 - wet season	6	0.1	0.028	0.0104
	Site 8 - dry season	8	0.5	0.132	
	Site 8 - wet season	6	0.1	0.003	0.0138
Overall baseflow vs. stormflow conditions for different seasons	Dry season - baseflow	23	1.0	4.098	
	Dry season - stormflow	32	3.3	46.482	0.0736
	Wet season - baseflow	24	0.1	0.048	
	Wet season - stormflow	24	0.8	4.772	0.1468
Overall baseflow vs. stormflow conditions	Baseflow	47	0.5	2.156	
	Stormflow	56	2.2	29.750	0.0289
Overall dry vs. wet seasons	Dry season	55	2.3	29.722	
	Wet season	48	0.5	2.474	0.0190

Table 4-4: Nitrogen composition of the greatest TN found at Haytons Stream.

Date sampled	17/02/2016	15/03/2016	15/03/2016	31/03/2016	23/06/2016
Site	4	3	4	4	3
Season	Dry	Dry	Dry	Dry	Wet
Flow conditions	Stormflow	Stormflow	Stormflow	Baseflow	Stormflow
TN (mg/L)	12.7	46.8	38.2	19.9	26.3
PON (mg/L), portion	3.7, 29%	0.6 ,1 %	0.6, 2%	0.3, 1%	0.3, 1%
DON (mg/L), portion	4.6, 36%	31.1, 67%	26.0, 68%	10, 50%	10.7, 41%
NO_X-N (mg/L), portion	1.2, 10%	1.5, 3%	1.2, 3%	0.9, 5%	1.3, 5%
NH_4-N (mg/L), portion	3.2, 25%	13.6, 29%	10.4, 27%	8.7, 44%	14.0, 53%

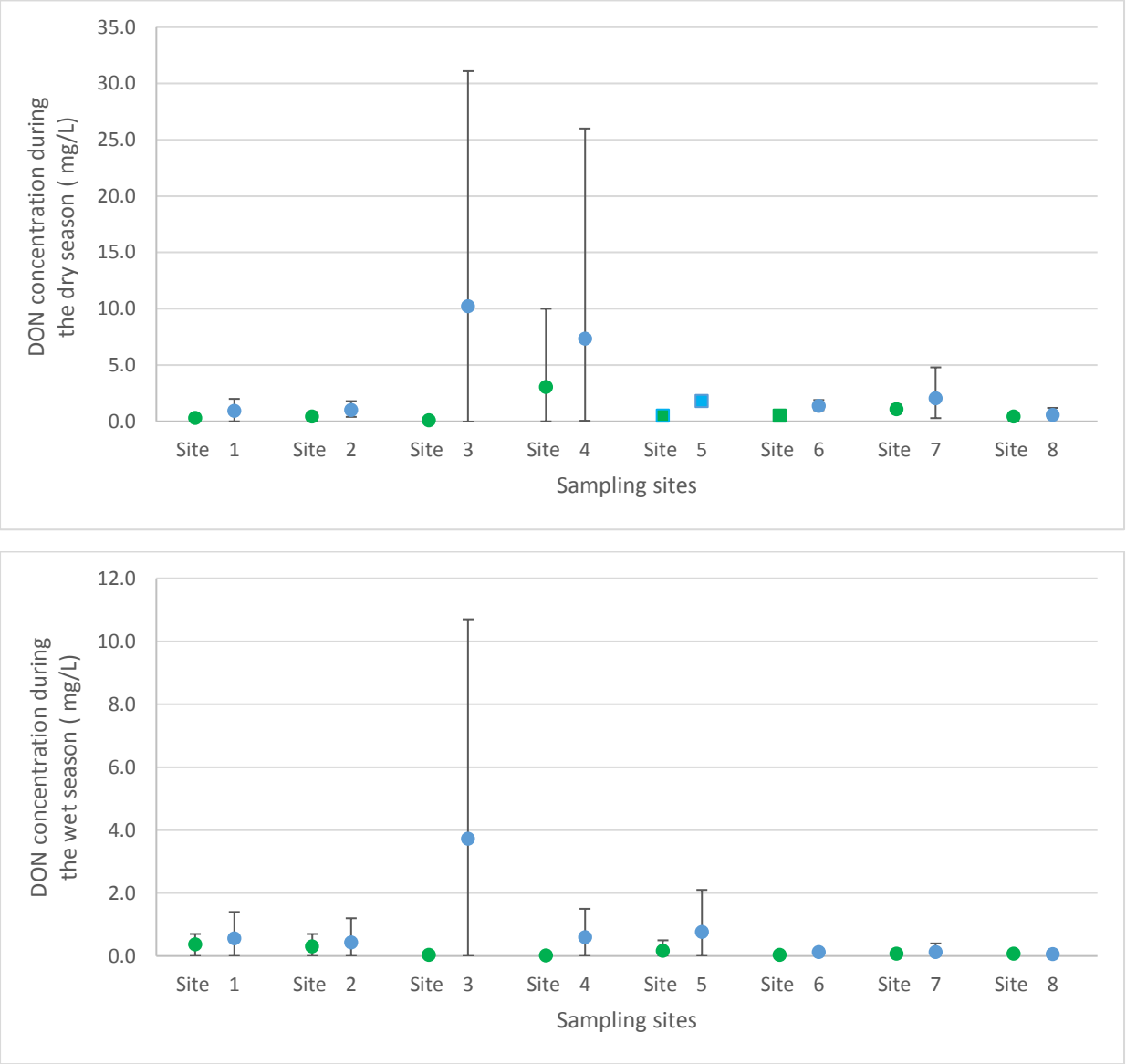


Figure 4-4: Dissolved organic nitrogen concentrations along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.4 Ammoniacal nitrogen

Ammoniacal nitrogen (NH_4-N) concentration had a similar variation along Haytons Stream as TN and DON, increasing from Site 1 to 3 and decreasing downstream. Between Sites 2 and 3, the mean concentration increased from 0.6 mg/L to 3.6 mg/L and between Sites 7 and 8 it decreased from 1.4 mg/L to 0.3 mg/L (Table 4-5).

There was a significant difference between upstream Sites 1 and 2 as well as downstream Sites 5 and 6. In addition to that, flow conditions also had significant influence in NH_4-N concentrations at those sites but no relation was found regarding seasons (Table 4-5).

Highest peaks in NH_4-N concentrations were also found at Sites 3 and 4, with concentrations going up to 14.0 mg/L. NH_4-N levels at Site 8 were found to be the lowest along Haytons Stream, with significant difference compared to Site 1 (Figure 4-5; Table 4-4; Table 4-5).

A very significant difference was found between the overall NH_4-N concentrations along Haytons Stream under baseflow and stormflow conditions, with concentrations in NH_4-N being more than double under stormflow conditions. Although this difference was not significant during the dry season, it was very significant during the wet season (Table 4-5).

Regarding the dry and wet seasons, there was a decrease in mean NH_4-N concentration, but was not statistically significant. At Site 7 a very significant difference was found, with mean concentration in NH_4-N being considerable lower during the wet season compared to the dry season (Table 4-5).

Table 4-5: Summary of t-test results with mean concentrations of NH_4-N between sites, flow conditions and seasons; p-values shows the difference between the current row and the row above; red p-values represent a very relevant difference and yellow a relevant difference.

Criteria	Site and/or condition	Number of samples	Mean NH_4-N (mg/L)	Variance	P-value
Individual Sites	Site 1	14	0.5	0.236	
	Site 2	15	0.6	0.299	0.8815
	Site 3	12	3.6	25.349	0.0657
	Site 4	15	2.5	10.410	0.5190
	Site 5	8	1.2	1.256	0.1844
	Site 6	10	1.1	0.774	0.8435
	Site 7	15	1.4	1.488	0.5059
	Site 8	14	0.3	0.058	0.0036
Group of sites	Sites 1 and 2	29	0.6	0.259	
	Sites 3 and 4	27	2.9	16.641	0.0055
	Sites 5 and 6	18	1.1	0.929	0.0341
Flow conditions for a group of sites	Sites 3 and 4 - baseflow	12	1.4	6.187	
	Sites 3 and 4 - stormflow	15	4.2	22.556	0.0700
Season for a group of sites	Sites 3 and 4 - dry season	15	3.3	17.546	
	Sites 3 and 4 - wet season	12	2.5	16.651	0.6385
Seasons for Individual sites	Site 7 - dry season	9	1.6	3.813	
	Site 7 - wet season	6	0.1	8.042	0.0104
Overall baseflow vs. stormflow conditions for different seasons	Dry season - baseflow	23	1.1	0.300	
	Dry season - stormflow	32	1.9	9.054	0.2563
	Wet season - baseflow	24	0.5	2.079	
	Wet season - stormflow	24	1.8	8.320	0.0445
Overall baseflow vs. stormflow conditions	Baseflow	47	0.8	6.306	
	Stormflow	56	1.9	5.023	0.0199
Overall dry vs. wet seasons	Dry season	55	1.6	0.236	
	Wet season	48	1.2	0.299	0.3803

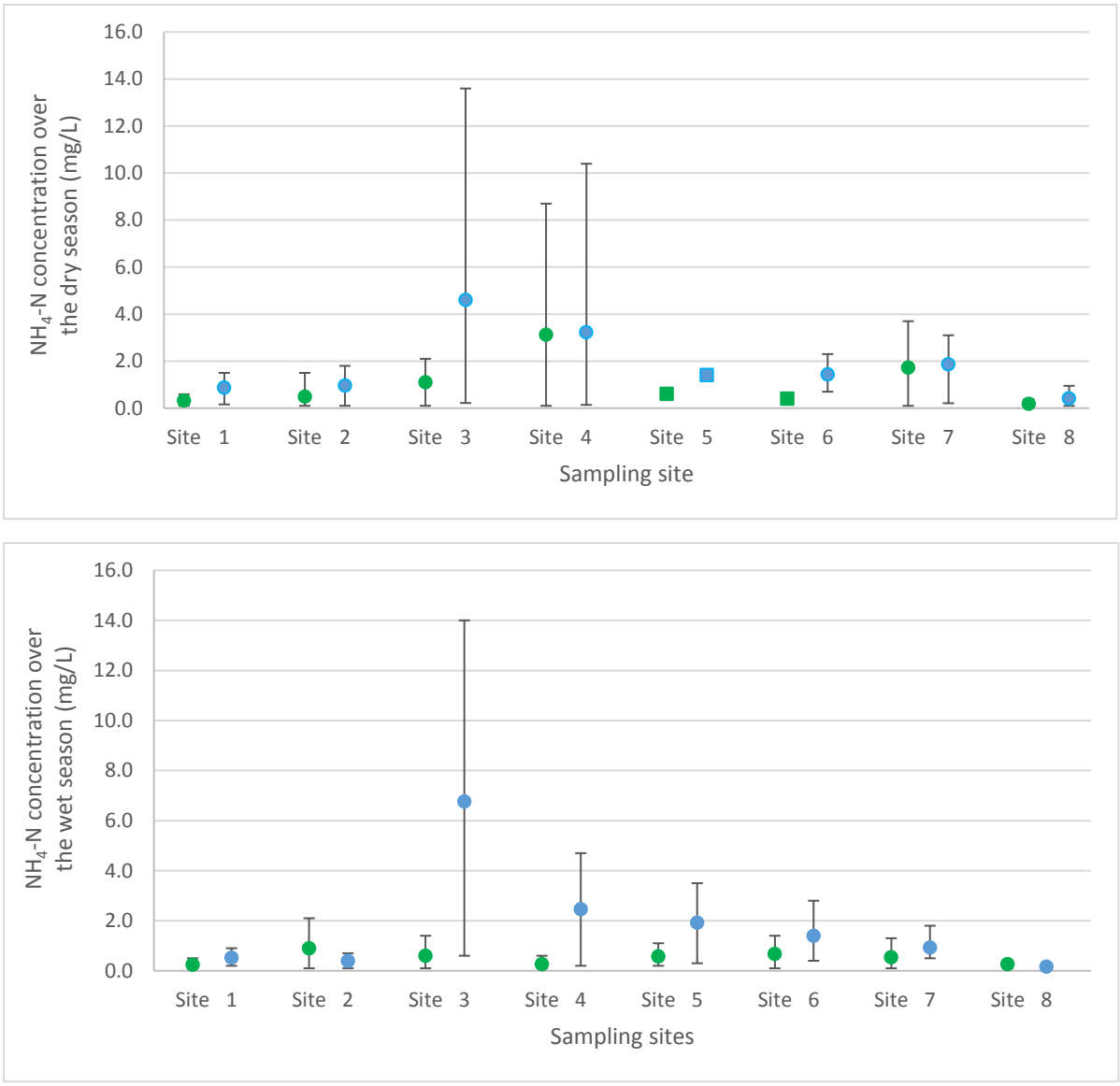


Figure 4-5: Ammoniacal nitrogen concentrations along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.5 pH and NH_4-N toxic levels

According to the Canterbury Land & Water Regional Plan, values of pH should be between 6.5 and 8.5 (Canterbury Regional Council, 2015). Values of pH were found higher than 8.5 only at the upper part of Haytons Stream. Levels of pH lower than 6.5 were found along Haytons in all sites, mainly during the dry season (Figure 4-6).

Variation in pH values were observed to be higher at the upper part of Haytons' and lower at the lower part. At the upper part of Haytons, Sites 1 and 2, mean pH was found to be 7.5 with a variance of 0.9164 while at the lower part of Haytons, Sites 7 and 8, mean pH was 7.0 with a variance of 0.2097 (P=0.0258), an statistical significant difference. No significant difference between seasons and flow conditions were found along Haytons Stream (Figure 4-6).

Crossing information of pH values and NH_4-N concentrations along Haytons Stream, toxic concentrations in NH_4-N were found (Canterbury Regional Council, 2011). During the dry season, the most critical toxic concentrations were found at the middle and upper part of the stream together with Site 7 (Figure 4-7).

During the wet season, samples exceeding the toxicity levels of NH_4-N were found once at Sites 1, 2, 5 and 6 and twice at Sites 3 and 4. Sites 7 and 8 did not have any sample exceeding the toxicity levels for NH_4-N.

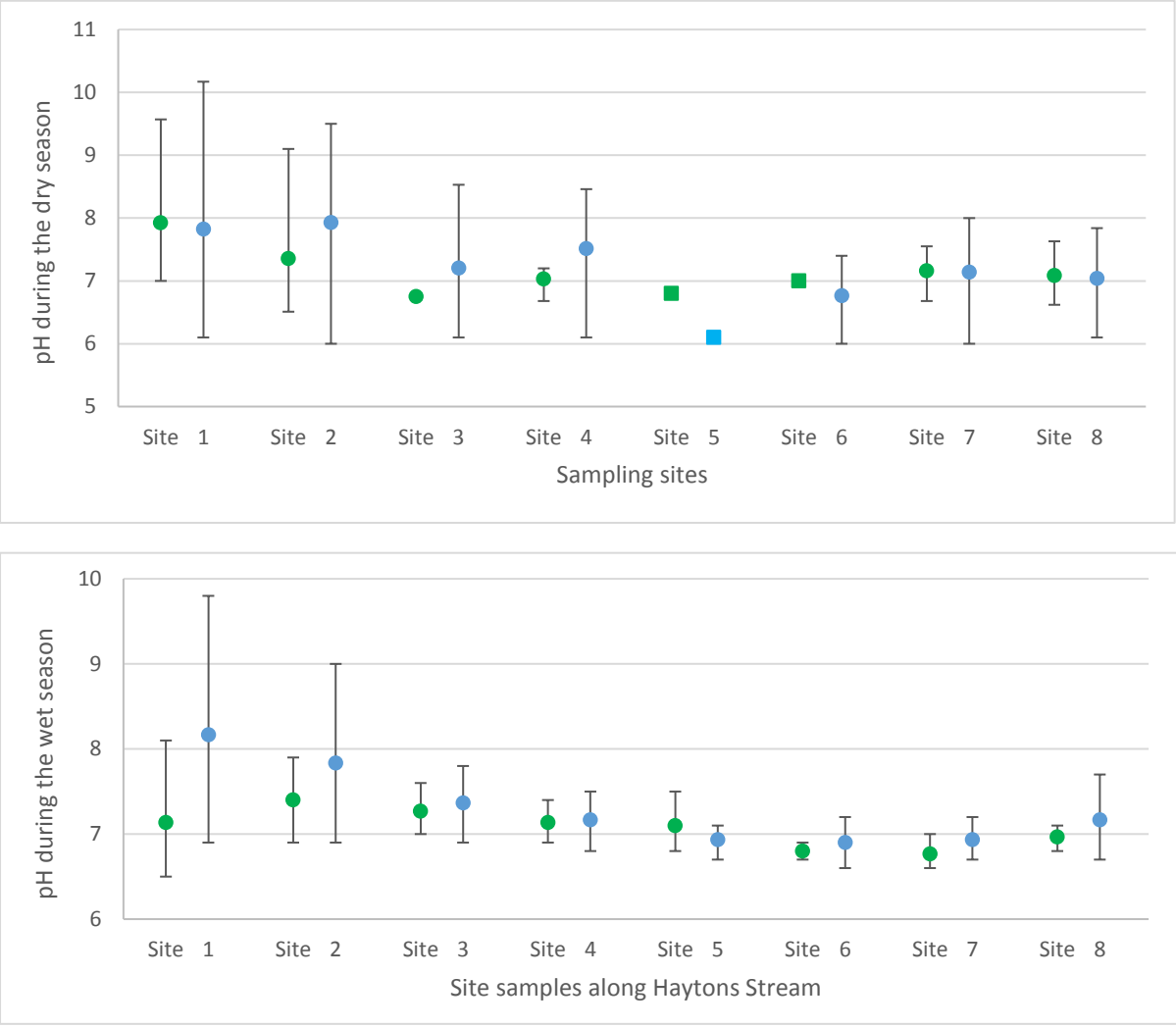


Figure 4-6: pH values along Haytons Stream along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

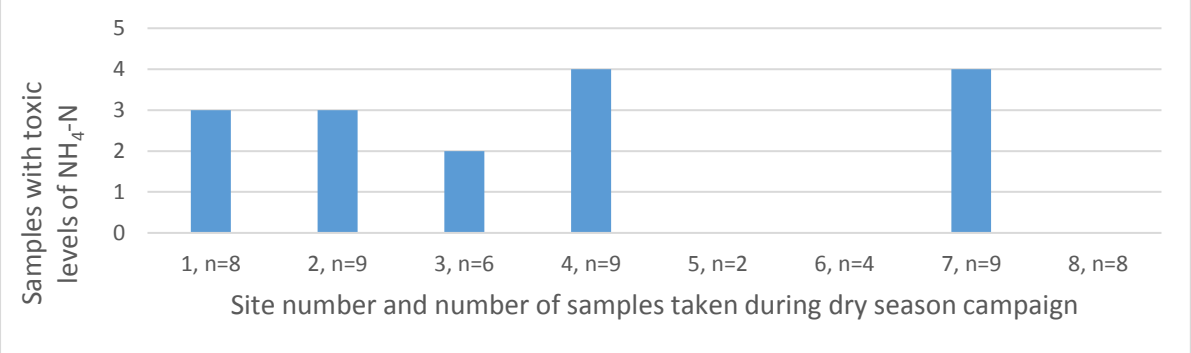


Figure 4-7: Number of samples with concentration equal to or higher than the toxic levels of NH4-N during the dry season.

4.6 Oxidized nitrogen

More than ninety percent of the samples had oxidised nitrogen (NO_X-N) concentrations above the trigger value of 0.444 mg/L (ANZECC, 2000). The only significant difference in NO_X-N concentrations was found between Sites 3 and 4: Site 3 had a mean concentration of 1.3 mg/L while Site 4 had 0.8 mg/L (P=0.0083). Site 3 was also found to have the greatest concentration in NO_X-N of 2.2 mg/L and the lowest concentration of 0.2 mg/L was found at Site 8 (Figure 4-8).

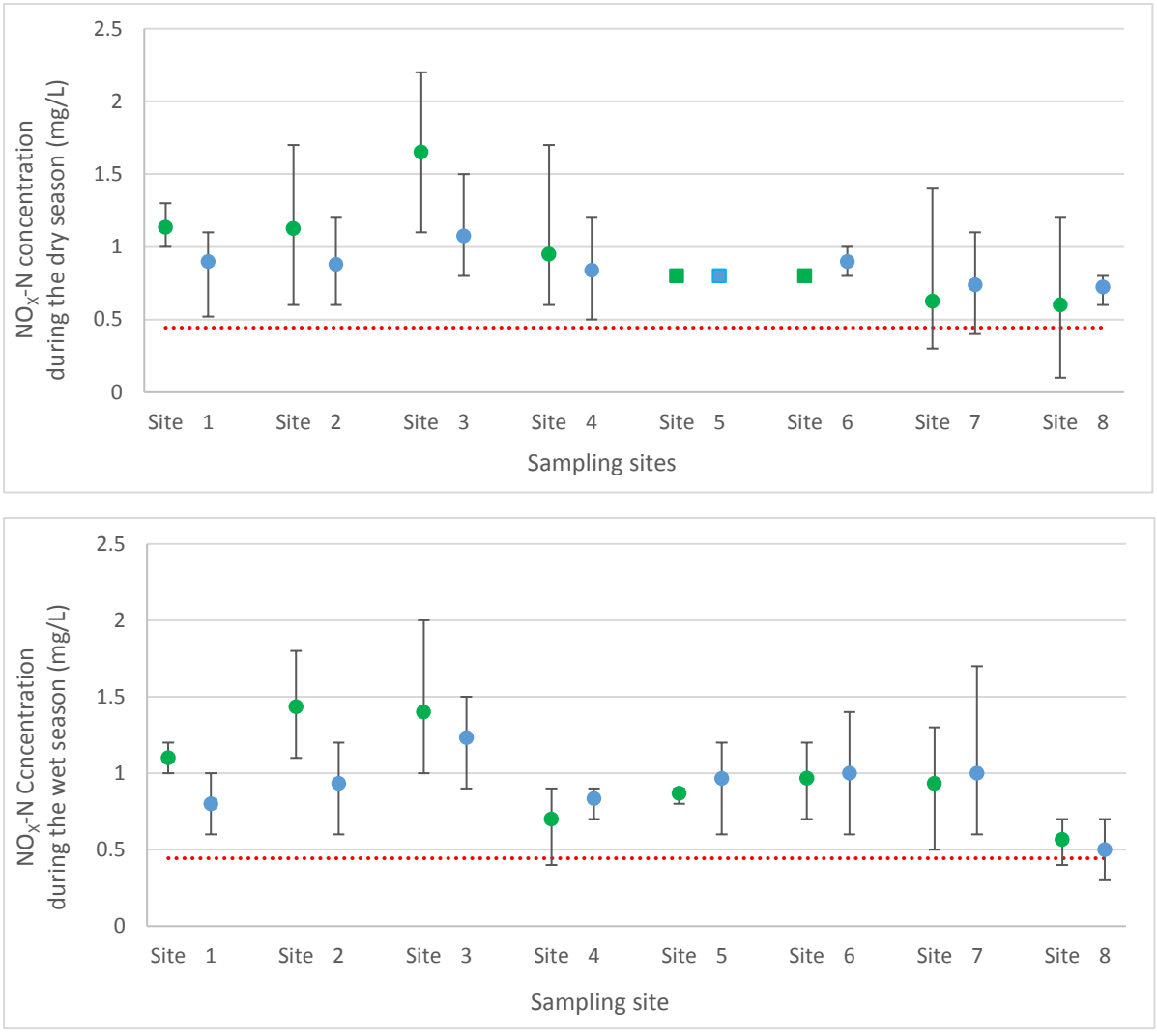


Figure 4-8: Oxidized nitrogen concentrations along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). ANZECC trigger value of 0.444 mg/L in red dotted line and a square represents sampling with only one sample.

4.7 Temperature

Temperature values along Haytons Stream did not significantly change during the same season along Haytons Stream, except for some localized fluctuation (Figure 4-9). During the dry season, temperature ranged between 8 and 21 °C and overall, there was no significant difference was found between sites. Lowest temperatures were found at Sites 4 and 8, which could be related to the characteristics of those sites. During the wet season, temperatures were between 6 and 11°C. Overall, under baseflow conditions the mean temperature was 12.0°C and under stormflow conditions 13.8°C (Figure 4-9, Table 4-6). The mean dry season temperature was 16.7°C and the mean wet season temperature was 9.2 °C, with greater fluctuation in temperature values over the dry season (Table 4-6).

Table 4-6: Summary of t-test results with mean temperatures between sites, flow conditions and seasons; p-values shows the difference between a row and the row above; red p-values represent a very relevant difference and yellow a relevant difference.

Criteria	Site and/or condition	Number of samples	Mean Temp. (°C)	Variance	P-value
Overall baseflow vs. stormflow conditions for different seasons	Dry season - baseflow	23	16.0	12.862	
	Dry season - stormflow	32	17.2	5.854	0.1515
	Wet season - baseflow	24	8.3	2.389	
	Wet season - stormflow	24	9.2	2.085	0.0392
Overall baseflow vs. stormflow conditions	Baseflow	47	12.0	22.346	
	Stormflow	56	13.8	20.171	0.0595
Overall dry vs. wet seasons	Dry season	55	16.7	8.995	
	Wet season	48	8.8	2.404	4.59E-29

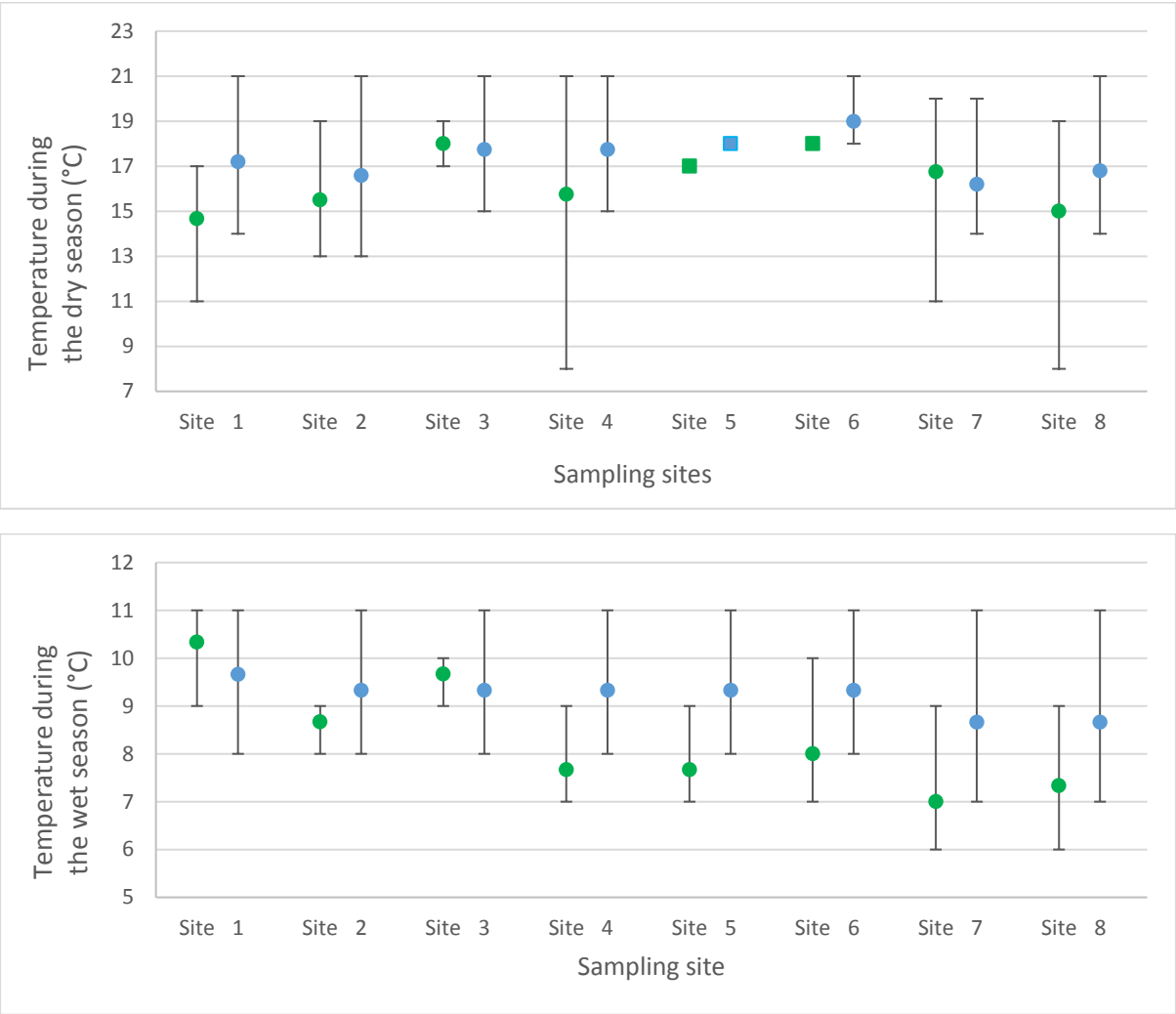


Figure 4-9: Temperature along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.8 Conductivity

The conductivity values fluctuated and there was no statistical difference between sites at Haytons Stream. Site 3 was found to have the highest peak conductivity, mean conductivity (125.7 µS/cm) and highest variation (variance of 3706.64). Conductivity found at Haytons Stream was found to be above guideline value of 175 µS/cm (Biggs, 2000) at some sites but the majority of the samples were below this value (Figure 4-10).

The only significant difference found was regarding the flow conditions during the dry season, with mean conductivity of 117.0 µS/cm and variance of 1025.42 under baseflow conditions while under stormflow conditions was 99.2 µS/cm and variance of 1082.3 (P=0.0632).

Elevated TN concentrations were found to be related with high conductivities. Samples taken on 28/10/2015, 24/03/2016, 31/03/2015, 23/06/2016, 29/06/2016, 08/07/2016 and 11/07/2016 had the highest conductivities linked to the highest TN concentrations during that sampling campaign (Appendix).

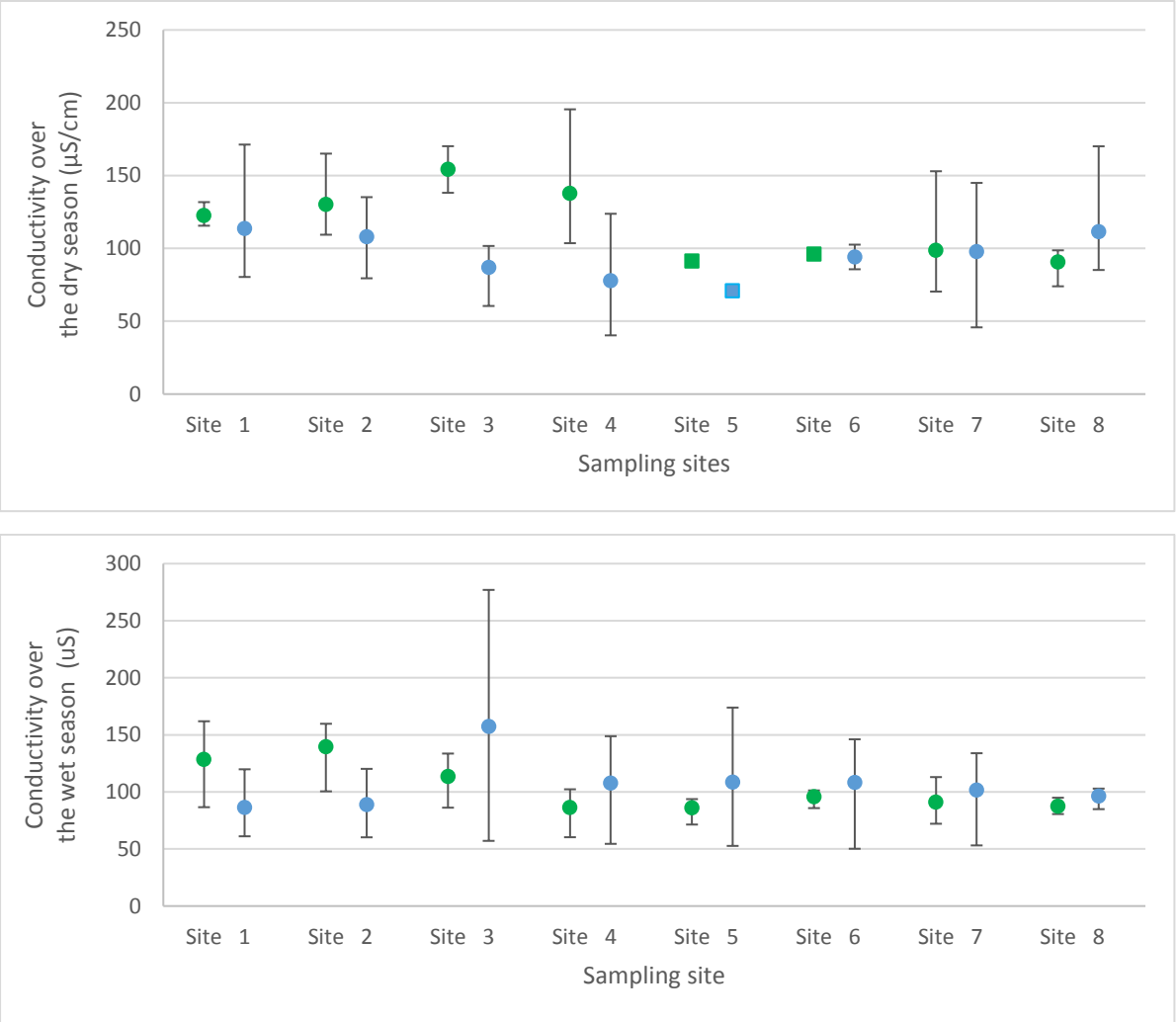


Figure 4-10: Conductivity along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.9 Turbidity

Most of the turbidity values found at Haytons Stream were higher than 5.6 NTU, the ANZECC (2000) trigger level for lowland rivers in New Zealand. Turbidity values decreased along Haytons Stream, with highest levels and variances were found at the upper part of Haytons and the lowest at the lower part. Although no significant difference was found between sites along Haytons Stream, comparing Sites 1 and 8 it was very evident the decrease in turbidity levels (Figure 4-11, Table 4-7)

Comparing baseflow versus stormflow for the dry and the wet seasons, a significant difference in turbidity values was found in both cases. During the wet season the levels of turbidity had a greater variation, and mean values, for the same flow condition, were similar. Overall baseflow versus stormflow, the difference was more significant and highlight a greater variation during stormflow conditions. No difference was found between the dry and wet seasons (Table 4-7).

During the dry season under baseflow conditions, the highest concentrations of TN were related to the highest turbidity, as was the case for sampling campaign on 09/09/2015, 03/02/2016 and 01/03/2016 in other words, 3 out of 4. Even though this relationship was found, the difference between the turbidity and concentration for those cases were irrelevant (Appendix).

Table 4-7: Summary of t-test results with mean values of turbidity between sites, flow conditions and seasons; p-values shows the difference between a row and the row above; red p-values represent a very relevant difference.

Criteria	Site and/or condition	Number of samples	Mean turbidity (NTU)	Variance	P-value
Individual sites	Site 1	14	22.6	212.182	
	Site 8	14	13.0	392.597	0.0531
Overall baseflow vs. stormflow conditions for different seasons	Dry season - baseflow	23	8.5	66.474	
	Dry season - stormflow	25	44.2	1580.895	0.0002
	Wet season - baseflow	24	11.8	144.732	
	Wet season - stormflow	24	44.9	2427.588	0.0037
Overall baseflow vs. stormflow conditions	Baseflow	47	10.2	107.013	
	Stormflow	49	44.5	1953.783	2.4166E-6
Overall dry vs. wet season	Dry season	48	27.1	1163.007	
	Wet season	48	28.3	1537.189	0.8663

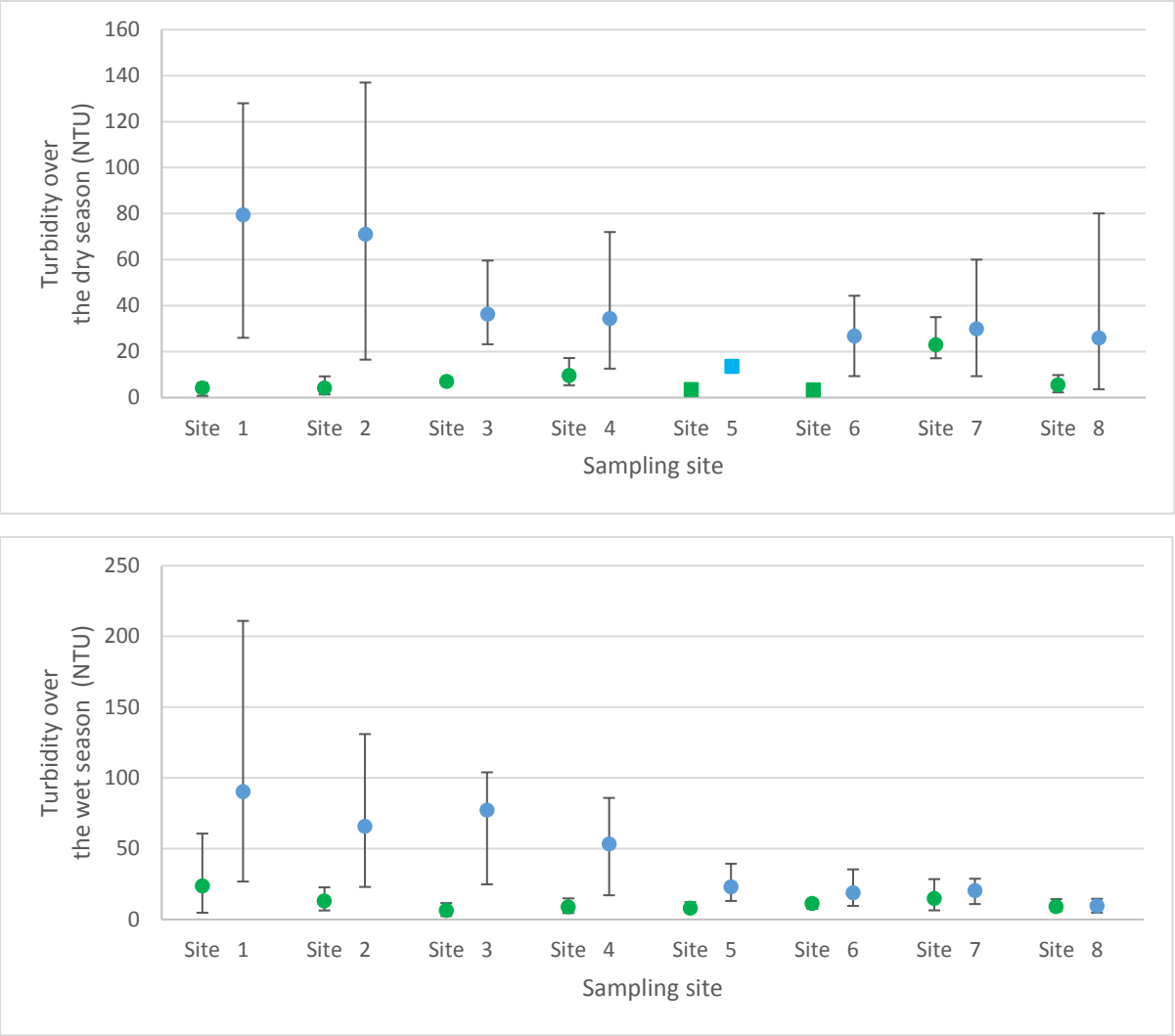


Figure 4-11: Turbidity along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.10 Dissolved oxygen

Dissolved oxygen (DO) concentrations along Haytons Stream were significantly different only between Sites 5 and 6, with the highest concentrations found at Sites 1 and 8. Most of the sites had DO concentration above ANZECC trigger value of 70%, only Site 5 was found to have a mean DO concentration below 70% (Table 4-8, Figure 4-12).

Regarding flow conditions, differences in the mean concentration were observed. This difference was significant during the wet season, with mean concentration under baseflow conditions was found below 70%, and not significant during the dry season (Table 4-8).

Comparing dry and wet seasons, difference was relevant with mean concentration was found to be higher during the dry season than during the wet season (Table 4-8).

Table 4-8: Summary of t-test results with mean values of dissolved oxygen between sites, flow conditions and seasons; p-values shows the difference between a row and the row above; red p-values represent a very relevant difference and yellow a relevant difference.

Criteria	Site and/or condition	Number of samples	Mean DO (%)	Variance	P-value
Individual sites	Site 1	12	82.9	121.902	
	Site 2	13	78.5	223.269	0.4033
	Site 3	11	79.6	193.455	0.8439
	Site 4	12	76.0	200.546	0.5413
	Site 5	7	64.1	264.810	0.1367
	Site 6	9	78.4	133.278	0.0770
	Site 7	13	75.1	211.077	0.5524
	Site 8	13	83.7	162.224	0.1226
Overall baseflow vs. stormflow conditions for different seasons	Dry season - baseflow	18	76.8	249.712	
	Dry season - stormflow	32	83.2	144.887	0.1435
	Wet season - baseflow	24	69.0	221.085	
	Wet season - stormflow	16	82.4	38.129	0.0004
Overall baseflow vs. stormflow conditions	Baseflow	42	72.4	242.577	
	Stormflow	48	83.0	107.877	0.0004
Overall dry vs. wet season	Dry season	50	80.9	188.099	
	Wet season	40	74.4	189.221	0.0281

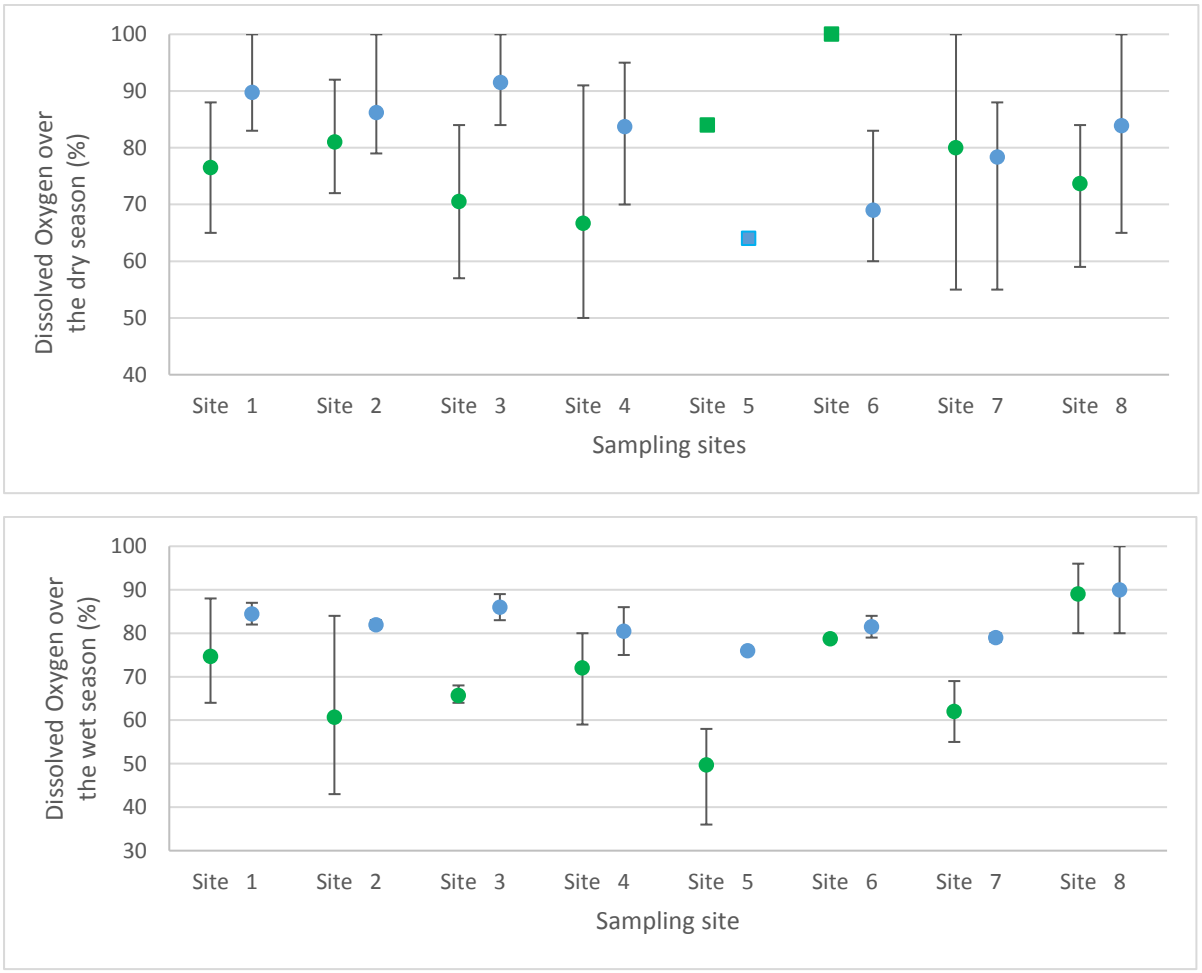


Figure 4-12: Dissolved oxygen along Haytons Stream under baseflow (green) and stormflow (blue) conditions during the dry (top graph) and the wet seasons (bottom graph). A square represents sampling with only one sample.

4.11 Street runoff

Levels of nitrogen compounds and other parameters in street runoff were lower than those found in Haytons Stream, especially conductivity and turbidity. Percentage of each nitrogen compound were similar than in some of the analyses and/or sites (Table 4-9, Figure 4-2).

These samples were collected at different times of a rain event. Samples collected on 28/10/2015 and on 15/3/2016 were collected during the steady state, where contaminants are more diluted. The sampled collected on 17/2/2016 was collected during the first flush, when contaminants are more concentrated in the street runoff (Table 4-9).

Table 4-9: Street runoff analyses from Site 2.

Date	28/10/2015	17/2/2016	15/3/2016
pH	No data	6.7	7.2
Turbidity (NTU)	15.4	No data	No data
Conductivity (uS/cm)	17.9	No data	No data
TN (mg/L)	1.3	2.1	1.8
PON (mg/L), percentage of TN	0.1, 8%	1.2, 57%	0.1, 6%
DON (mg/L), percentage of TN	0.4, 31%	0.1, 5%	0.5, 28%
NO_X-N (mg/L), percentage of TN	0.1, 8%	0.5, 24%	0.6, 33%
NH_4-N (mg/L), percentage of TN	0.7, 53%	0.3, 14%	0.6, 33%

4.12 River bed sediments

Initial results of river bed sediments analysis showed low concentrations of nitrogen and total carbon (see appendix). However, during a routine re-test of the sediment samples, an increase of NH_4-N was observed in a sample collected at Site 3 (Figure 4-13).

This sample was collected on 26/11/2015, analysed on 8/12/2015 and retested on 23/12/2015, analyses on 31/12/2015 and 8/01/2016 were performed in duplicate. The sample was wet (around 38% of dry mass) and it was kept in a 4°C chiller until drying (Figure 4-13).

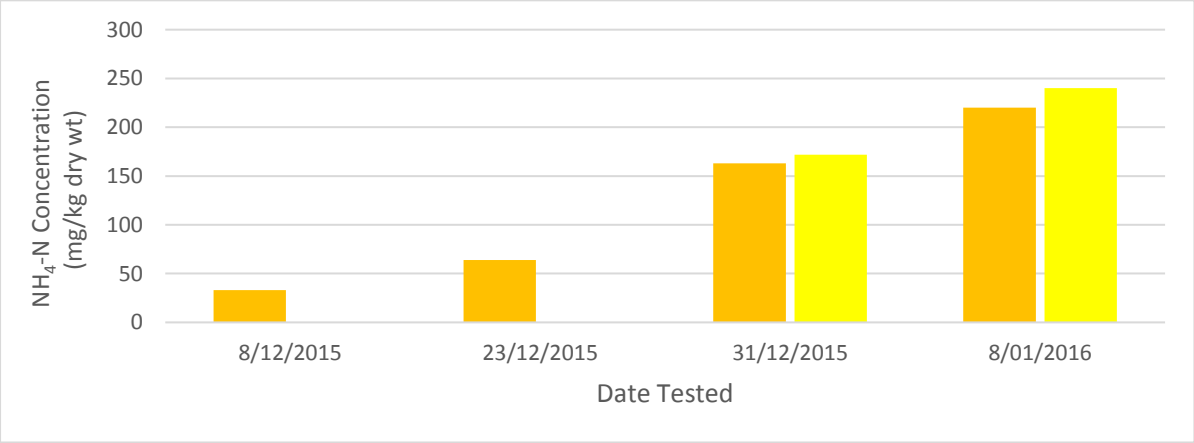


Figure 4-13: Release of NH_4-N reported from Hills Lab.

4.13 River bed incubation experiment

Due to the NH_4-N release reported from Hills Lab, a laboratory based experiment were performed to verify the release of NH_4-N under typical conditions. When the sample was taken, the NH_4-N concentration was found to be 18.1 mg/kg of dry sediment. After 4 weeks, it increased to 53.3 mg of NH_4-N per kg of dry sediment, almost 3 times more than the initial concentration (Figure 4-14).

Although this experiment confirmed previous results from an accredited laboratory, the increase in NH_4-N reported by the laboratory was much greater than this experiment. The method used by Hills lab to analyse NH_4-N in soil was different than the method used in University of Canterbury Laboratory.

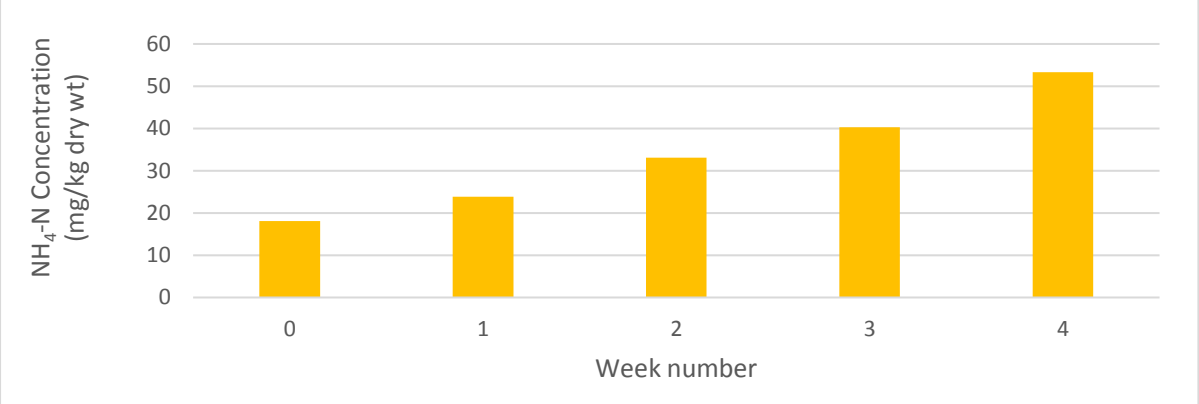


Figure 4-14: Changes in NH_4-N concentrations during river bed incubation experiment.

4.14 Water column incubation experiment

A water column incubation experiment was performed with water and sediments taken from Site 4. When the water was tested, it had a TN concentration of 34.1 mg/L, which was one of the highest this study had ever found at that time. After a month period, the TN concentrations dropped to 18.1 mg/L with the experiment A and to 20.0 mg/L with the experiment B (Figure 4-15).

The NO_X-N concentration remained stable though time. Concentrations of DON decreased, possibly due to the ammonification process which converts organic nitrogen in ammonia. Even though organic nitrogen was converted as ammonia, NH_4-N concentration decrease (Figure 4-15).

The only nitrogen compound that increased concentration was PON, which was visible as an algal bloom as the solution became green at the second week (Figure 3-14). The pH was 6.6 at the day of collection and increased to 9.8 after four weeks (Appendix).

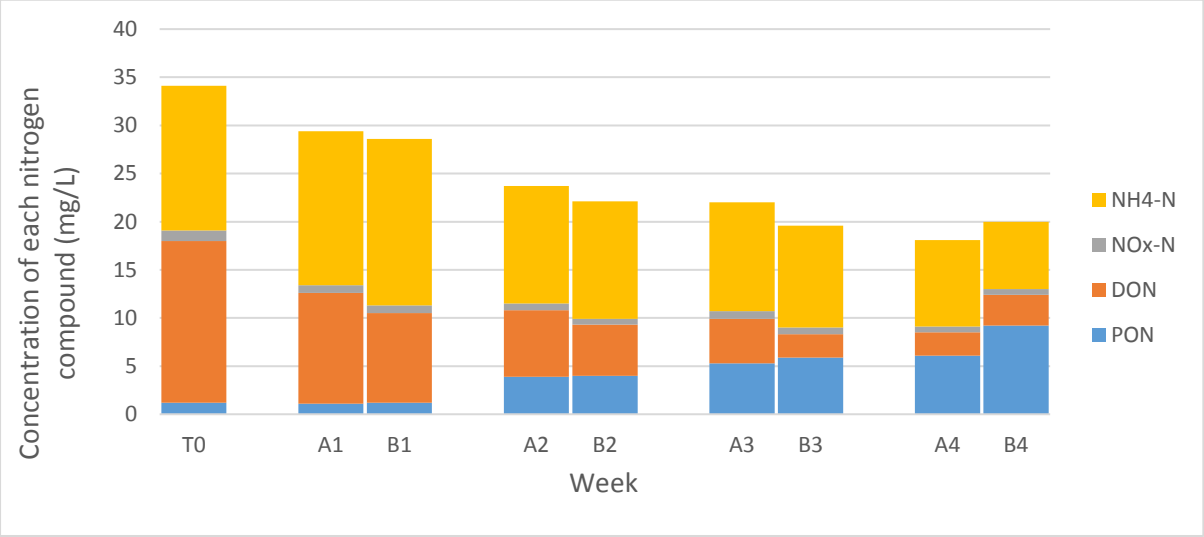


Figure 4-15: Concentrations of each nitrogen compounds along time during the long-term study A and B with sediment plus water containing high nitrogen compounds concentration.

5 Discussion

The results presented in Chapter 4 are discussed in this chapter with an emphasis on the main findings of this research.

5.1 Transformation of nitrogen compounds

At the upper part of Haytons Stream, the majority of nitrogen was found in its inorganic form (i.e. NH_4-N & NO_X-N). At Sites 3 and 4, peak concentrations of DON and NH_4-N shifted nitrogen dynamics, leading to changes in water quality parameters (Figure 4-4).

When DON reaches the waterways it is converted into NH_4-N through a process called ammonification (Figure 2-3). This process happens in both aerobic and anaerobic zones of reed beds, in water, stream bed sediments, and riparian zones (Lee et al., 2009). NH_4-N is then converted into NOx-N due to the nitrification process (Eq.1 and 2). This is an aerobic process carried out by microorganisms which due to its highly oxygen demanding nature, it occurs in a zone close to the surface where oxygen concentration is high (Ahn, 2006). Kinetically, ammonification proceeds more rapidly than nitrification (Ryzhakov et al., 2010). Furthermore, high concentrations of NH_4-N were produced at those sites, resulting in most of the toxic levels of NH_4-N that were found at Haytons Stream (Figure 4-6).

Taking into account the high concentrations of NH_4-N at Site 5, that rates of ammonification are faster than nitrification, and the fact that nitrification is a highly oxygen demanding reaction, it was to be expected that the lowest values of DO along Haytons Stream were found at Site 5, with a mean concentration below 70%. This is strong evidence that NH_4-N has been converted into NO_X-N at Site 5, due to a statistically significant increase of oxygen downstream as well as a decrease in DON and NH_4-N values (Table 4-8; Figure 4-4; Figure 4-5).

Levels of NO_X-N had a significant decline only between Sites 3 and 4. The high concentration at Site 3 could be the result of nitrification process happening at that site. However, the decrease in NO_X-N observed at Site 4 could be more related to dilution than to any other factor, given that this is where Haytons Streams merges with Paparua Stream (Figure 4-8).

In general, NO_X-N concentrations were found to be above the ANZECC trigger value of 0.444 mg/L in more than 90% of the samples along Haytons, but still much lower than the NPS-FM toxic annual median value of 6.9 mg/L (ANZECC, 2000; Ministry for the Environment, 2014).

At the lower part of Haytons the majority of nitrogen was found in its organic form, which is a heterogeneous mix of compounds that varies widely in space and time within the aquatic environment (Berman & Bronk, 2003). This organic nitrogen can be related to biota, cyanobacteria, algae, and microorganisms in general that live in water and sediments. Through biological processes these organisms uptake simple nutrients and convert them into complex organic structures using photosynthesis, in the case of the autotrophs. These organisms are very important in wetlands because they convert and uptake nitrogen compounds. The availability of nutrients, sun incidence, and retention time at the WRB create ideal conditions to promote growth of these organisms.

A study of the composition of nitrogen compounds in two streams located in a mixed forest/dairy rural catchment in Japan observed mean concentrations of TN much lower than found in Haytons Stream (1.34 mg/L with n=21; 0.95 mg/L with n=23). The majority of nitrogen were found in its inorganic form and DON concentrations were found greater than PON (Hayakawa et al., 2006). Haytons Stream had concentration of DON higher than PON during the dry season and lower during the wet season (Figure 4.2).

In natural freshwaters the majority of nitrogen is in its organic form, and the concentration of DON is normally between 5 to 10 times higher than PON. The ratio of DON:PON tends to decrease when it becomes eutrophic (Krupka, 1989; Wetzel, 2001). Haytons Stream was found to be in contrast to that, with the majority of nitrogen found in its inorganic form and concentrations of PON similar to or higher than DON in most parts of the stream during the wet season (Figure 4.2).

This study found a significant decrease in TN before and after the wetland, highlighting the effectiveness of this wetland in treating the water. Mean removal of TN was 54% ($P=0.0067$), as well as 80% removal of NH_4-N ($P=0.003$) and 69% removal of DON ($P=0.0389$). NO_X-N and PON had a decrease in mean concentrations but was not statistically significant.

Notwithstanding the above benefits, it is important that the organisms responsible for removing nitrogen compounds stay in the wetland, given the potential harm they could cause downstream if in high

concentrations. It is desirable that organisms (algae) which retain nitrogen are removed before they leave the wetland. Removing algae and other organisms in the ponds would consequently decrease nitrogen loads in the Heathcote River, due to the fact that PON represented between 30% to 60% of the nitrogen compounds at the output of the WRB (Site 8).

Due to the availability of light and nutrients algae reproduce at a very fast rate. When they die organic matter accumulates in the water. The first step of decay is ammonification, which releases ammonia, a very harmful substance at elevated pH levels, as mentioned before. In addition, the nitrification process is a highly oxygen demanding process, resulting in hypoxic conditions. This situation was observed during some sampling campaigns along Haytons Stream (Figure 5-1).

Algae bloom was also noticed during the water column incubation experiment, as evidenced by “green colour”, after two weeks of incubation (Figure 3-14). Levels of PON increased while DON and NH_4-N decreased, suggesting that the microorganisms that are responsible for decreasing levels in nitrogen compounds are also increasing in concentration, similar to what happens at the WRB (Figure 4-2).

Comparing the water column incubation experiment with the concentration of nitrogen compounds downstream Site 3 along Haytons Stream, both had similar dynamics. Nitrogen compounds concentrations decreased over time/ downstream, especially DON and NH_4-N, and PON increased overtime (Figure 4-1; Figure 4-2; Figure 4-15).

Figure 5-1: Algae bloom at Site 4, picture taken on 25/11/2015.

5.2 Differences between baseflow and stormflow conditions

Baseflow and stormflow conditions had evident differences in water quality parameters, with an increase in turbidity, dissolved oxygen, temperature, and nitrogen compounds concentrations occurring under stormflow conditions. Under stormflow conditions rainwater washes the urban surface, carrying rubbish, pollutants, organic matter, metals and other contaminants. When the street runoff is discharged in the waterways it increases water flow, creating a turbulent condition. As turbulence mixes stream water with street runoff, air and stream bed sediments increase in turbidity and dissolved oxygen, both of which had the greatest mean concentrations under stormflow conditions (Table 4-7; Table 4-8).

Contribution of street runoff to the nitrogen loads was also observed, with nitrogen concentration being greater during the first flush. Most nitrogen compounds were found in particulate form during the street-runoff first flush while NH_4-N was found to be the main nitrogen compound during the steady-state, when street runoff is more diluted (Table 4-9).

Water temperature also changes under the influence of rainfall. Rainfall flows to streams mostly from impervious surfaces, which are dominated by concrete and galvanized roofs, asphalt and concrete

pavements in the Haytons catchment. During rainfall events the heat accumulated on impervious surfaces transfers to the rain water, which goes to the waterways as street runoff, increasing the stream's water temperature. Although this increase was not significant during the dry season, it was significant in overall stormflow conditions and very significant during the wet season (Table 4-6).

TN, PON, DON and NH_4-N also had higher concentrations during stormflow events (Figure 4-1; Figure 4-3, Figure 4-4; Figure 4.5). PON and DON are organic nitrogen, which in a waterway is mostly retained in the riparian zone, stream bed sediments, and also inside stormwater pipelines. Due to the turbulent state of the flow, those compounds are released and mix with the stream water. The increase in organic nitrogen was very significant under stormflow conditions and the increase in DON observed in this study was much greater at Sites 3 and 4 than any other site (Table 4-2; Table 4-3; Table 4-4).

NH_4-N is a result of the ammonification process that occurs mainly in bed sediments and inside the stormwater pipe network, where organic matter is retained. Because ammonium is a positively charged ion, it is held relatively strongly by the ion-exchange bond occurring at the surfaces of organic matter in soils, being adsorbed by the stream bed sediments (Zhang et al., 2016). Under stormflow conditions, stream bed sediments are mixed and NH_4-N is released resulting in mean concentrations doubling under stormflow conditions (Table 4-5).

Samples taken on 31/03/2016 under baseflow conditions had similar turbidity values for Sites 1 and 3 (5.3 NTU and 5.7 NTU, respectively), but DON was much greater at Site 3 (0.1 mg/L at Site 1 and 10.0 mg/L at Site 3). Samples taken on 23/06/2016 under stormflow conditions had a turbidity at Site 1 of 211 NTU and 103 NTU at Site 3. However, DON concentrations were 1.5 mg/L at Site 1 and 10.7 mg/L at Site 3. This difference highlights that DON concentrations are not always related to turbidity.

These results of NH_4-N along Haytons Stream were similar to those found on a previous study at Site 2 that found an evident increase in NH_4-N concentrations under stormflow conditions, compared to baseflow conditions (O'Sullivan & Charters, 2014). An increase in NO_X-N concentration under stormflow conditions was noticed during the monitoring in 2013, but it was not observed in this study (Figure 4-8).

A study conducted in Melbourne, Australia, compared the concentration of nitrogen compounds in urban baseflow and storm events. The mean value of 2.15 mg/L in total nitrogen was similar in both base flow and stormflow conditions. In addition, the concentration of NH_4-N and PON was found higher under stormflow than in baseflow conditions and concentrations of NO_X-N and DON were found lower (Taylor et al., 2005). These results were partially different from the values found at Haytons Stream: TN, PON, NH_4-N and DON were found to increase under stormflow conditions and there was no significant difference regarding NO_X-N concentrations with flow conditions (Figure 4-1; Figure 4-3, Figure 4-4; Figure 4.5; Figure 4-8).

5.3 Differences between the dry and the wet seasons

The main differences between the dry and wet seasons were observed in dissolved oxygen concentration and stream water nutrient dilution.

Sunlight helps autotroph organisms synthesize food in the photosynthesis process. Accordingly, this conversion process is higher during summer time, the dry season in New Zealand. To be able to synthesize food these organisms require nutrients which can be obtained from soils and/or water, and most of the nitrogen uptake by plants is in its inorganic form (NO_X-N and/or NH_4-N). Photosynthesis also results in the production of oxygen in the aquatic environment.

Although oxygen solubility increases with lower temperatures, lower DO concentrations were observed during the wet season (i.e. winter) compared to the dry season (i.e. summer). The mean DO concentration in the wet season was 69.0% under baseflow conditions compared to 76.8% during the dry season (Table 4-8). This increase in DO concentration during the dry season can be related to a higher photosynthetic activity of the microorganisms and plants in the stream, which uptake nutrients and increase DO concentrations. The dry season and elevated stream water temperature acts in favour of biological processes, especially the processes that occur in soils and in the drainage system which can be partially responsible for NH_4-N concentrations (Memon & Butler, 2002). Additionally, it helps processes such as nitrification and denitrification, increasing its conversion rates. However, those rates essentially cease at temperatures greater than 45 °C (Kadlec & Reddy, 2001).

During nineteen years of data in a meso-eutrophic lake in Israel, the seasonal change observed was mostly regarding DON and NO_X-N. In winter, concentration of DON was found to decrease to 39% of TN and NO_X-N increased to 29%. During summer time, DON was found to represent 65% of TN and NO_X-N around 4%. Concentrations of NH_4-N and PON remained similar (4% and 27% respectively) along the year (Berman & Bronk, 2003). Although this represents a lake environment, it highlights the changes in nitrogen compounds in summer periods in the aquatic ecosystem.

Stream dilution was verified during the wet season, when the mean TN concentration in Haytons was 58 % lower than during the dry season. The most noticeable example of this happened at Site 4 during the wet season, when very low TN concentrations, sometimes even below detections limits, were observed (Table 4-4). This site is where Paparua merges with Haytons Stream and over the wet season more water was flowing from Paparua Stream.

Dilution could also be the reason why toxic levels of NH_4-N were found 16 times during the dry season but only 8 during the wet season (Figures 4-5; Figure 4-6; Table 4-5). That is to say, dilution helps improve water quality parameters in the wet season.

In addition, it was noted that during the dry season when the frequency of rainfall is much lower than in the wet season, the differences in TN concentration between baseflow and stormflow conditions were greater than during the wet season. Low frequency of rain means more atmospheric deposition. Rubbish and pollutants can also accumulate on the city's surfaces and wash away during rain events, often entering straight into urban streams (Table 4-1).

5.4 Identification of point discharges

During this study, changes in water quality parameters such as turbidity and conductivity together with an elevation in all nitrogen compounds mean concentrations were noticed at Sites 3 and 4 (Figure 4-1; Figure 4-3; Figure 4-4; Figure 4-5; Figure 4-8). These changes suggest that point discharges happen upstream and/or at those two sites.

This situation had already been reported in previous studies conducted at Haytons Stream (ECan, 2007; Moores et al., 2009). However, an unexpected finding in this study was the frequency of discharges.

Elevated TN concentrations were found in 5 out of 9 sampling campaigns during the dry season and 3 out of 6 campaigns over the wet season at Sites 3 and 4 (Appendix 1).

Another unusual situation was the percentage of DON in these point discharges, which dramatically changed the balance of nitrogen compounds (Figure 4-2). In addition, 98% of the DON found in a sampling at Site 3 was in Urea form, which could also be responsible for elevated DON concentration in others sampling campaigns (Appendix 2).

Ammonification is a biological process which converts organic matter to ammonia and is conducted mostly by fungi and prokaryotes and is influenced by temperature, pH, C/N ratio, and availability of nutrients (Vymazal, 2007). The stream bed incubation experiment showed a threefold increase in NH_4-N during the ammonification process in a month period under typical outdoor conditions (Figure 4-14). The increase in NH_4-N reported by Hills lab was even greater, sevenfold over a month period, which is believed to be the result of a high concentration of DON in the sediment.

It is unlikely that the NH_4-N concentrations found together with elevated DON were a result of the ammonification process, because of the low rates of biological processes. For some of the peaks in DON concentrations the turbidity was low, suggesting that both NH_4-N and DON elevated concentrations at Site 3 came from point discharges.

Given the nature of the sampling campaigns, all sampling dates for baseflow conditions happened randomly. The biggest concern would be whether point discharges are happening on a daily basis and how much of the discharges get into Haytons Stream.

Other types of contaminants, such as oils, hydrocarbons and a considerable amount of rubbish were found at Haytons Stream waterways, that are likely contributed by the local population or industries contributes to this situation. A drone video footage on 18/04/2016 observed a car truck being washed just five metres from Haytons Stream between Sites 1 and 2 and its runoff going straight to the stream without any treatment. This is of concern because of the wide range of polluting substances trucks can transport and be washed off with soap or detergents ending up in the stream without any treatment.

Similarly, during a walk along Haytons Stream on 23/11/2015, traces of discharge were found on the stream bed, precisely between Sites 4 and 3, where it was verified that floor wash-off from a factory entered a piped outlet and it was discharged straight to the stream.

Furthermore, many intermediate bulk containers (IBC) or pallet tanks, labelled as Hydrochloric acid, were piled up less than two metres from the waterway. There was no spillway designed, and in case of an accident, earthquake, or a mishandling by an operator, this substance would certainly end up in the stream.

5.5 Riparian zones, retention and detention ponds

This study found a decrease in TN concentrations from the middle to the lower part of Haytons Stream, showing that concentrations of nitrogen compounds decrease along the stream (Figure 4-1). This decrease can be related to the retention ponds along the stream together with the recently planted riparian zone and a wetland at the lower part of the catchment.

Riparian zones are the transition zone from terrestrial to aquatic habitat, which produces variation in the moisture, redox potential, and organic matter conditions that support denitrification (Cirmo & McDonnell, 1997). In addition, the potential for denitrification is typically highest in surface soils, where organic C is available (Gold et al., 2001; Hedin et al., 1998).

The new development of Haytons Stream catchment from Site 4 to Site 6 demonstrated an improvement in some water quality parameters, such as decreasing turbidity and nitrogen concentrations. The riparian zone and the creation of retention ponds along Haytons increased soil permeability and the surface area of the stream in contact with atmosphere that contains oxygen. Thus it increases the detention time of the stream water and the contact of water and sun, increasing water temperatures. With increasing temperature in wetlands, there is an increase in the removal of TN and NO_X-N (Kadlec & Reddy, 2001).

This new development with a restored stream waterway contrasts with a small and not-well-maintained riparian zone between Sites 1 and 4. During this study it was observed that parts of the riparian zone along Haytons Stream were in poor condition, especially between Sites 3 and 4, where part of the retaining wall was collapsed at some points and about to fall at other parts. The collapse would

discharge sediments, rubbish, and potential harmful substances which were currently stored near Haytons Stream waterways.

Wet retention ponds with filters were found to have a much higher retention of TN and NO_X-N compared to the ones without a filter, with an average TN retention of 9.5% for wet ponds and 57.6% for a wet pond with filters, for NO_3^- 12.7% of retention for wet pond to 78.5% for wet pond with filters. For NH_4-N retention was -21.5% for wet pond and -7.7% for wet pond with filters. For suspended solids, a wet pond was found to reduce 11.1% and for wet pond with filter 79.2% (Sønderup et al., 2015).

During the analysis it was found that part of the turbidity was due to the presence of green algae in water, especially at Site 8, where most of the samples were of green colour. Taking into account data from Sønderup et al. (2015) showing that a filter could have a big impact on the nitrogen removal, this approach would reduce PON being discharged from the WRB, decreasing considerably the nitrogen loads into Heathcote River (Figure 4-2).

Site 7 was found to have an inconsistency in nitrogen compounds concentration. During the dry season, parts of Haytons Stream were found dry. Between Sites 1 and 2, Sites 6 and 7, and Sites 7 and 8, no water flow was observed during long dry periods. Site 7 was found to have the worst situation, because there was no inflow or outflow over a long period without rainfall (Figure 5-2). Collins et al. (2010) pointed out that while wet ponds decrease the TN concentrations from a mean concentration of 1.7 mg/L to 1.4 mg/L, dry ponds tend to increase in a higher proportion from 1.2 mg/L to 2.1 mg/L. This data could explain the fluctuation in nitrogen compounds concentration at Site 7 and also the increase in TN along Haytons (Table 4-1; Figure 5-2).

Over the past year detention basins were built along Haytons Stream to store excess stormwater. These detention basins help to decrease peak flows at Haytons Stream, holding water temporarily in order to mitigate flood risks in the catchment. In addition, these detention basins increase pollutant removal by physical settling of suspended solids, which include particle-bound pollutants such as nutrients, heavy metals and hydrocarbons. However, there is only grass planted and those detention basins do not take advantage of other varieties of plants that could increase permeability, nutrient and heavy metals uptake as well as having a better environment for birds and other species.

Figure 5-2: Left picture shows Haytons Stream waterways between Sites 1 and 2 over the dry season and right picture shows Site 7 with almost no water.

An approach for detention basin design is the Blue-Green City concept, which aims to recreate a naturally oriented water cycle while contributing to the amenity of the city by bringing water management and green infrastructure together. This concept is carried out by combining and protecting the hydrological and ecological values of the urban landscape while providing resilient and adaptive measures to deal with flood events (Thorne, 2016).

The blue-green concept includes the use of a bioretention system which combines both a variety of vegetation and underlying filter media for removal of pollutants. The vegetation, which covers the system's surface, increase the filtration process as well as maintains its porosity, while the filter media removes sediments, heavy metals, and suspended solids when the storm water passes through (Mangangka et al., 2016). In addition, the use of a variety of plants would create a more diverse environment, contributing to the local fauna and flora.

Using this concept, the detention basin would not just retain water for a short period, it would also treat the water by a number of physical, chemical, and biological processes, providing a multitude of environmental, ecological, socio-cultural and economic benefits.

5.6 Treating discharges

It is known that biological processes do not tolerate drastic changes in temperature, pH, and concentration of nutrients. Retention ponds help to buffer the pH and nutrients concentration, promoting

a better environment for biological processes. According to our data, pH and nutrients concentration have a lower variability at the middle and lower part of the stream, where retention ponds exist (Figure 4-7; Table 4-1; Table 4-2; Table 4-3; Table 4-5).

The denitrification process converts nitrate into nitrogen gas (Eq. 2), and is carried out by bacteria and controlled by the availability of carbon, ideal pH, temperature and residence times (Knowles, 1982). The wetland was found to aid in stabilising the stream's pH and temperature, due to the large storage capacity and residence times, which provides better conditions to promote denitrification processes than other sites at Haytons Stream (Figure 4-7; Figure 4-9).

TN concentrations were found to be lower at Site 8 compared to Site 1, showing that even though TN concentrations increased along Haytons, the series of retention pond plus the WRB helped decrease TN concentrations to the lowest levels along Haytons Stream (Table 4-1).

Together with the processes that occur in the retention ponds, plants uptake and volatilization of ammonia contributes to the decrease of nitrogen loads and concentration in the stream. Comparing concentrations of TN, NH_4-N, DON and NO_X-N along the stream, it was evident the contribution of retention ponds and wetland on the reduction of all forms of nitrogen, except for PON (Table 4-1; Table 4-2; Table 4-3; Table 4-5; Figure 4-8).

Stream water quality was evaluated through two different grassland catchments and it was observed that the potential of denitrification processes was greater in the wetland compared to the grassland and riparian forest (Hayakawa et al., 2006).

The restoration of a hypertrophic lake with treatment performed by a wetland was investigated. The main nitrogen compound was PON (64%) and the wetland was designed to reduce PON loads. Total nitrogen loads were reduced just by reducing PON loads. However, an increase of DON, NH_4-N, and NO_X-N was observed (Coveney et al., 2002).

A similar approach was conducted in a eutrophic lake in which PON represented around 58% of the total nitrogen. The main biochemical mechanism for PON removal was found to be sedimentation and it was seasonally dependent. Removal of PON was 78 ± 10% (mean ± SD) and 24 ± 9% for TN, showing an increase of other nitrogen compounds (Dunne et al., 2013).

Although these studies showed that it is possible to reduced nitrogen loads in Heathcote River by reducing PON loads, other nitrogen compounds could increase in concentrations.

5.7 Dry season – disconnection of ponds

During the dry season, it was observed that there was no water flow connecting all the ponds along Haytons stream. In fact, it was noticed that part of Haytons had no surface water flowing, leading us to believe that part of Haytons Stream is also an underground stream (Figure 5-3).

Groundwater and surface water are nearly always linked (White et al., 2001). Mandel (1974) demonstrated the relationship between groundwater levels in groundwater-fed rivers in the Canterbury Plains. With lower groundwater levels during the dry season, its contribution to the surface water is smaller, explaining why parts of Haytons Stream has no water flow during dry weather. Thus, with a lower groundwater table, stream water with elevated nitrogen concentration might leach into the groundwater, contaminating and decreasing its water quality and, in some cases, making it unsuitable for drinking.

A press release on July 2016 reported that the Christchurch City Council had shut down a contaminated water bore near central Christchurch after two spikes in nitrate levels (Stylianou, 2016). This bore was located around 2.5 km from Haytons Stream, where in terms of TN the stream is within the worst 25% of similar sites in New Zealand (LAWA, 2016). There is no evidence that this situation could be related to Haytons Stream, due to the distance. Despite this it is possible for nitrogen to leach to the groundwater, especially nitrate and nitrite, affecting surrounded areas.

The impact of urbanization on the biogeochemistry of streams at the groundwater–surface water interface was investigated. It was observed that levels of NO_3^- in the groundwater were lower where more dissolved organic carbon (DOC) were available, suggesting that denitrification and removal of NO_3^- in groundwater were limited by DOC availability (Mayer et al., 2010).

There is very little information about DOC availability and TN concentration in Haytons Stream catchment groundwater. Increasing concentrations of nitrogen compounds in the groundwater is a worldwide problem and mitigating the nitrogen compounds concentrations in the waterways would help to decrease this problem locally.

6 Conclusions, recommendations and future research

6.1 Conclusions

Composition of nitrogen compounds along Haytons Stream:

Different levels of nitrogen compounds were found along Haytons Stream. Total nitrogen concentration was found to increase from the upper to the middle part of Haytons, and to decrease downstream, with the lowest levels found at the lowest part of the stream (i.e. at the output of Wigram Retention Basin). Most of the nitrogen was found to be in its dissolved form along the stream (DON, NH_4-N, and NO_X-N), but mainly in its particulate form at the discharge of the Stream.

In the middle part of Haytons Stream the concentration of total nitrogen increased drastically. This increase, especially in DON and NH_4-N concentrations, changed the proportion of nitrogen compounds. This situation led to toxic concentrations of ammonia in the middle part of Haytons. Levels of NO_X-N were found to exceed the ANZECC trigger value in 90% of samples.

The variation in the composition of nitrogen compounds were driven mostly by point discharges which were found to increase nitrogen concentrations and change nitrogen composition. The series of treatment systems along Haytons Stream were also found to be responsible for decreasing nitrogen concentrations as well as converting inorganic nitrogen to organic nitrogen.

Change in nitrogen compounds with flow conditions and season:

Flow conditions were found to affect the dynamics of nitrogen compounds, with higher concentrations of PON, DON and NH_4-N in all sites under stormflow conditions. Likewise, processes that occur in the stream bed sediments and inside the stormwater pipe network were found partially responsible for increasing NH_4-N concentrations under stormflow conditions. Furthermore, street runoff was found to contribute to the nitrogen loads.

Differences in nitrogen compounds between seasons were also noticed. During the wet season lower concentrations of PON, DON and NH_4-N were found during both baseflow and stormflow conditions, mainly caused by higher rain incidence as well as the contribution of a higher groundwater table. In contrast, during the dry season, an increase in sun incidence, water temperature and photosynthesis

contributed to biological processes such as ammonification, nitrification, and denitrification, which were found to increase nitrogen removal along Haytons Stream.

The highest change in nitrogen compounds were found during the dry season, with the nitrogen concentration and composition changing drastically under stormflow conditions.

Factors affecting the dynamics of nitrogen compounds in Haytons Stream:

Point discharges are a major source of DON and NH_4-N in the middle part of Haytons. Point discharges need to be dealt with through education and policy in order to improve Haytons Stream health. Consciousness of the local population, companies and workers, together with enforcement by local authorities of pollution prevention measures are necessary to improve Haytons Stream health. Point discharges that increase the nitrogen levels significantly need to be identified and minimized or eliminated to improve the health of Haytons Stream.

Retention ponds, riparian planting, and wetlands were found to be efficient in improving water quality parameters such as pH and turbidity as well as at nitrogen removal and conversion, decreasing levels of DON and NH_4-N along Haytons Stream and increasing PON at the lower part, where the wetland is located. Improved design of these treatment systems would allow nitrogen compounds to be converted to easier-to-treat forms of nitrogen (i.e. PON). In addition, management of PON exiting Wigram Retention Basin could decrease nitrogen loads entering Heathcote/Opawaho River from 30% to 60%.

6.2 Recommendations

Based on the findings of this research, some recommendations for improving Haytons Stream health is proposed:

- Identify and cease point discharges from industries at Haytons Stream in order to minimize nitrogen compounds entering Haytons Stream. Based on this study, a relationship between elevated TN concentrations and conductivity was found, which can help future monitoring at Haytons Stream to track where point discharges are coming from.

- Manage the high concentration of ammonia in key parts of streams by implementing measures to oxygenate the water. This is necessary to promote the nitrification process and to minimize

ammonia toxic levels as well as have a healthier stream.

- Identify discharges from roads, car parks, and other land uses that enter the stream without any treatment. Treatment of street runoff before entering Haytons Stream is necessary to decrease nitrogen loads under stormflow conditions and discharges on impervious surfaces.

- Improve the design of Wigram Retention Basin in order to retain particulate forms of nitrogen (PON) minimizing nitrogen loads into the Heathcote River. A high percentage of PON is currently being discharged into the river.

- Extend riparian zone plantings between Sites 1 and 4 to improve water quality, aesthetics, and overall stream health.

- Ensure the community is well informed that discharges occurring at Haytons Stream will end up at Heathcote River. Engagement of the local community and companies with the preservation of Haytons Stream waterways would help to improve the health of the stream.

6.3 Future research

- Studies of nitrogen compounds in groundwater at Haytons Stream are necessary in order to ensure that nitrogen compounds are not contaminating surrounding groundwater.

- Assessment of the relationship between sediments, carbon and nitrogen with the increase of nitrogen compounds in the waterways.

- Expand the studies to phosphorus, carbon, heavy metal, and sediments in Haytons Stream.

- Evaluation of the treatment processes of nitrogen compounds in the stream bed sediments, wetland, riparian zone and stormwater network and how to improve denitrification process in urban streams.

- Develop a model to simulate the dynamics of nitrogen compounds with stream water surface, flow, temperature, retention time, groundwater level, rain, sun incidence, and other factors that would help to better understand nitrogen compounds processes in urban streams.

References

Ahn, Y-H 2006, 'Sustainable nitrogen elimination biotechnologies: A review', *Process Biochemistry,* vol. 41, no. 8, pp. 1709-1721.

Allen, MB & Arnon, DI 1955, 'Studies on nitrogen-fixing blue-green algae. I. Growth and nitrogen fixation by Anabaena cylindrica Lemm', *Plant Physiology,* vol. 30, no. 4, p. 366.

ANZECC 2000, 'Australian and New Zealand guidelines for fresh and marine water quality', *National water quality management strategy paper,* vol. 4

APHA, A, WEF 1999, *Standard methods for the examination of water and wastewater*, American Public Health Association., Washington, U.S.A.

Berman, T & Bronk, DA 2003, 'Dissolved organic nitrogen: a dynamic participant in aquatic ecosystems', *Aquatic microbial ecology,* vol. 31, no. 3, pp. 279-305.

Bernhard, A 2010, 'The nitrogen cycle: Processes, players, and human impact', *Nature Education Knowledge,* vol. 2, no. 2, p. 12.

Biggs, BJ 2000, *New Zealand periphyton guideline: detecting, monitoring and managing enrichment of streams*, Ministry for the Environment.

Brush, GS 2009, 'Historical Land Use, Nitrogen, and Coastal Eutrophication: A Paleoecological Perspective', *Estuaries and Coasts,* vol. 32, no. 1, pp. 18-28.

Burns, RC & Hardy, RW 1975, *Nitrogen fixation in bacteria and higher plants*, Springer Verlag.

Carpenter, SR, Caraco, NF, Correll, DL, Howarth, RW, Sharpley, AN & Smith, VH 1998, 'Nonpoint Pollution of Surface Waters with Phosphorus and Nitrogen', *Ecological Applications,* vol. 8, no. 3, pp. 559-568.

Cirmo, CP & McDonnell, JJ 1997, 'Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review', *Journal of Hydrology,* vol. 199, no. 1, pp. 88-120.

Collins, KA, Lawrence, TJ, Stander, EK, Jontos, RJ, Kaushal, SS, Newcomer, TA, Grimm, NB & Cole Ekberg, ML 2010, 'Opportunities and challenges for managing nitrogen in urban stormwater: A review and synthesis', *Ecological Engineering,* vol. 36, no. 11, pp. 1507-1519.

Council, AC 2012, *River Water Quality Annual Report 2010*, State of the Environment Monitoring

Council, CR 2011, *Canterbury Natural Resources Regional Plan*, 978-1-927146-12-5.

Council, CR 2015, 'Canterbury Land & Water Regional Plan', *Policy,* vol. 1

Coveney, MF, Stites, DL, Lowe, EF, Battoe, LE & Conrow, R 2002, 'Nutrient removal from eutrophic lake water by wetland filtration', *Ecological Engineering,* vol. 19, no. 2, pp. 141-159.

Dalton, H & Brand-Hardy, R 2003, 'Nitrogen: The Essential Public Enemy', *Journal of Applied Ecology,* vol. 40, no. 5, pp. 771-781.

de Barros, MTL, Yazaki, LFO & Porto, MFA 2009, 'Recuperação da Qualidade da água do Reservatório Billings com o Sistema de Flotação do Rio Pinheiros'

Dunne, EJ, Coveney, MF, Marzolf, ER, Hoge, VR, Conrow, R, Naleway, R, Lowe, EF, Battoe, LE & Inglett, PW 2013, 'Nitrogen dynamics of a large-scale constructed wetland used to remove excess nitrogen from eutrophic lake water', *Ecological Engineering,* vol. 61, Part A, pp. 224-234.

ECan 2007, *Avon/Otakaro and Heathcote/Opawaho Rivers: Analysis of water quality data from 1992-2006*, PDP, Pattle Delamore Partners Ltd

Elliott, EM, Kendall, C, Wankel, SD, Burns, DA, Boyer, EW, Harlin, K, Bain, DJ & Butler, TJ 2007, 'Nitrogen Isotopes as Indicators of NOx Source Contributions to Atmospheric Nitrate Deposition Across the Midwestern and Northeastern United States', *Environmental Science & Technology,* vol. 41, no. 22, pp. 7661-7667.

Environment, Mft 2014, 'National Policy Statement for Freshwater Management 2014', no. ME 1202

FISRWG 1998, *Stream corridor restoration: principles, processes, and practices*, Federal Interagency Stream Resoration Working Group

Gold, AJ, Groffman, PM, Addy, K, Kellogg, DQ, Stolt, M & Rosenblatt, AE 2001, 'Landscape attributes as controls on ground water nitrate removal capacity of riparian zones', *Journal of the American Water Resources Association,* vol. 37, no. 6, pp. 1457-1464.

Groffman, PM, Boulware, NJ, Zipperer, WC, Pouyat, RV, Band, LE & Colosimo, MF 2002, 'Soil nitrogen cycle processes in urban riparian zones', *Environmental Science and Technology,* vol. 36, no. 21, pp. 4547-4552.

HACH 2003, *Water Analysis Handbook*, Hach company, Loveland, Colorado, U.S.A.

Hayakawa, A, Shimizu, M, Woli, K, Kuramochi, K & Hatano, R 2006, 'Evaluating stream water quality through land use analysis in two grassland catchments: Impact of wetlands on stream nitrogen concentration', *Journal of Environmental Quality,* vol. 35, no. 2, pp. 617-627.

Hedin, LO, Joseph, CvF, Ostrom, NE, Kennedy, BP, Brown, MG & Robertson, GP 1998, 'Thermodynamic Constraints on Nitrogen Transformations and Other Biogeochemical Processes at Soil-Stream Interfaces', *Ecology,* vol. 79, no. 2, pp. 684-703.

Johnson, PTJ, Townsend, AR, Cleveland, CC, Glibert, PM, Howarth, RW, McKenzie, VJ, Rejmankova, E & Ward, MH 2010, 'Linking environmental nutrient enrichment and disease emergence in humans and wildlife', *Ecological Applications,* vol. 20, no. 1, pp. 16-29.

Kadlec, RH & Reddy, KR 2001, 'Temperature Effects in Treatment Wetlands', *Water Environment Research,* vol. 73, no. 5, pp. 543-557.

Kaushal, SS, Groffman, PM, Band, LE, Shields, CA, Morgan, RP, Palmer, MA, Belt, KT, Swan, CM, Findlay, SEG & Fisher, GT 2008, 'Interaction between Urbanization and Climate Variability Amplifies Watershed Nitrate Export in Maryland', *Environmental Science & Technology,* vol. 42, no. 16, pp. 5872-5878.

Knowles, R 1982, 'Denitrification', *Microbiological reviews,* vol. 46, no. 1, pp. 43-70.

Krupka, HM 1989, 'Transformations of nitrogen forms in epilimnion of eutrophic Glebokie Lake (Masurian Lake District, Poland)', *Polskie Archiwum Hydrobiologii,* vol. 36, no. 1, pp. 29-96.

LAWA 2016, 'Haytons Drain at Retention Basin', https://www.lawa.org.nz/explore-data/canterbury-region/river-quality/heathcote-river/haytons-drain-at-retention-basin/.

Lee, C-g, Fletcher, TD & Sun, G 2009, 'Nitrogen removal in constructed wetland systems', *Engineering in Life Sciences,* vol. 9, no. 1, pp. 11-22.

Mandel, S 1974, *The groundwater resources of the Canterbury plains*, Lincoln College. New Zealand Agricultural Engineering Institute., 0075-952X.

Mangangka, IR, Liu, A, Goonetilleke, A, Egodawatta, P & SpringerLink 2016, *Enhancing the Storm Water Treatment Performance of Constructed Wetlands and Bioretention Basins*, Springer Singapore, Singapore.

Mayer, PM, Groffman, PM, Striz, EA & Kaushal, SS 2010, 'Nitrogen Dynamics at the Groundwater-Surface Water Interface of a Degraded Urban Stream', *Journal of Environmental Quality,* vol. 39, no. 3, pp. 810-823.

Memon, FA & Butler, D 2002, 'Identification and modelling of dry weather processes in gully pots', *Water Research,* vol. 36, no. 5, pp. 1351-1359.

Moores, J, Gadd, J, Wech, J & Flanagan, M 2009, *Haytons Stream catchment water quality investigation*, Niwa

O'Sullivan, A & Charters, F 2014, *Haytons Stream 2013 water quality investigation at Gerald Connolly Place*, University of Canterbury, Environment Canterbury Regional Council, 978-1-927299-37-1.

Perrie, AM, S; Milne, JR; Greenfield, S. 2012, 'River and Stream Water Quality and Ecology in the Wellington Region: States and Trends'

Ravishankara, AR, Daniel, JS & Portmann, RW 2009, 'Nitrous Oxide (N_20): The Dominant Ozone-Depleting Substance Emitted in the 21st Century', *Science,* vol. 326, no. 5949, pp. 123-125.

Ryzhakov, AV, Kukkonen, NA & Lozovik, PA 2010, 'Determination of the rate of ammonification and nitrification in natural water by kinetic method', *Water Resources,* vol. 37, no. 1, pp. 70-74.

Smil, V 1997, 'Global Population and the Nitrogen Cycle', vol. 277. SCI AMERICAN INC, NEW YORK, pp. 76-81.

Sønderup, MJ, Egemose, S, Hansen, AS, Grudinina, A, Madsen, MH & Flindt, MR 2015, 'Factors affecting retention of nutrients and organic matter in stormwater ponds', *Ecohydrology*

Strous, M, Fuerst, JA, Kramer, EH, Logemann, S, Muyzer, G, van de Pas-Schoonen, KT, Webb, R, Kuenen, JG & Jetten, MS 1999, 'Missing lithotroph identified as new planctomycete', *Nature,* vol. 400, no. 6743, pp. 446-449.

Stumm, W & Morgan, JJ 1995, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters,* Third edn, John Wiley & Sons.

Stylianou, G 2016, 'City council shuts down contaminated Wrights Rd water bore ', ed. T Press. The Press, http://www.stuff.co.nz/the-press/news/82281478/city-council-shuts-down-contaminated-wrights-rd-water-bore, 20/07/2016.

Taylor, GD, Fletcher, TD, Wong, THF, Breen, PF & Duncan, HP 2005, 'Nitrogen composition in urban runoff—implications for stormwater management', *Water Research,* vol. 39, no. 10, pp. 1982-1989.

Thorne, C 2016, 'Achieving urban flood resilience: the Blue-Green Advantage', in *Water New Zealand's Stormwater Conference 2016*. http://stormwaterconference.org.nz/programme/keynote-speakers-presentations/, Nelson, New Zealand, 18-20th May 2016.

Trimmer, M, Risgaard-Petersen, N, Nicholls, JC & Engstrom, P 2006, 'Direct measurement of anaerobic ammonium oxidation (anammox) and denitrification in intact sediment cores', *Marine Ecology Progress Series,* vol. 326, pp. 37-47.

Vesilind, PA & Morgan, SM 2004, *Introduction to Environmental Engineering*, Thomson Brooks/Cole, Belmont, Calif.

Vitousek, PM, Aber, JD, Howarth, RW, Likens, GE, Matson, PA, Schindler, DW, Schlesinger, WH & Tilman, DG 1997, *Technical Report: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences*, Ecological Society of America, 10510761.

Vymazal, J 2007, 'Removal of nutrients in various types of constructed wetlands', *Science of The Total Environment,* vol. 380, no. 1–3, pp. 48-65.

Wetzel, RG 2001, *Limnology: lake and river ecosystems*, Academic, London;San Diego, Calif;.

White, P, Clausen, B, Hunt, B, Cameron, S, Weir, J & Rosen, M 2001, 'Groundwater-surface water interaction', *Groundwaters of New Zealand*, pp. 133-160.

Wilcock, RJ, Nagels, JW, Rodda, HJE, O'Connor, MB, Thorrold, BS & Barnett, JW 1999, 'Water quality of a lowland stream in a New Zealand dairy farming catchment', *New Zealand Journal of Marine and Freshwater Research,* vol. 33, no. 4, pp. 683-696.

Zhang, L, Wang, S, Jiao, L, Li, Y, Yang, J, Zhang, R, Feng, S & Wang, J 2016, 'Effects of organic matter content and composition on ammonium adsorption in lake sediments', *Environmental Science and Pollution Research,* vol. 23, no. 7, pp. 6179-6187.

APPENDIX 1

Analyses Results

Dry Season

Samples collected on 9/09/2015 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (µS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1(12:30)	11	9.57	No data	6.34	120.0	2.1	2.0	1.1	0.59
Site 2(12:10)	13	9.10		9.24	165.1	4.0	4.0	1.66	1.5
Site 4 (11:55)	8	7.15		17.2	138.5	6.5	6.4	1.72	3.2
Site 7 (11:40)	11	7.55		19.0	153.0	6.6	6.5	1.44	3.7
Site 8 (11:30)	8	7.63		9.81	96.3	1.28	0.48	<0.002	<0.01

Samples collected on 28/10/2015 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (µS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NOx-N (mg/L)	NH_4-N (mg/L)
Site 1(14:45)	14.0	7.66	86	128	94.0	2.9	2.7	0.47	0.91
Site 2(13:22)	13.0	8.23	84	137	126.9	4.0	3.7	0.64	1.3
Site 2 runoff (13:30)	No data					1.28	1.15	0.113	0.66
Site 4(15:00)	13.5	7.51	88	60	145.0	4.4	4.5	0.45	1.4
Site 7(11:40)	13.5	6.98	96	80.1	170.1	5.8	5.0	0.79	1.8

Sediment samples collected on 26/11/2015

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Oxidation Reduction Potential (mV)	Conductivity (uS)	Total Nitrogen (g/100g dry wt)	Total Carbon (g/100g dry wt)	NO_X-N (mg/kg dry wt)	NH_4-N (mg/kg dry wt)
Site 1 (9:40 am)	16	7.4	13	1.22	177.8	0.25	4.0	<1.0	42
Site 2 upstream (9:25 am)	No data					0.14	1.81	<1.0	45
Site 2 (9:00 am)	17	7.4	34	1.47	153.3	0.33	6.5	<1.0	39
Site 4 (11:00 am)	18.5	7.6	93	1.71	78.3	0.27	4.5	<1.3	33

Samples collected on 28/01/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NOx-N (mg/L)	NH_4-N (mg/L)
Site 1(10:30)	15.6	10.17	>100	62.8	171.3	2.2	1.4	0.9	0.16
Site 2(10:45)	15.2	9.02	>100	16.5	90.7	1.9	1.4	0.9	<0.1
Site 3(11:15)	14.7	8.53	>100	23.2	60.5	1.5	1.0	0.8	0.22
Site 4(10:10)	14.8	8.46	95	12.6	40.3	1.8	0.7	0.5	0.14
Site 7(9:45)	15	8	81	12.4	45.8	1.5	0.9	0.4	0.21
Site 8(9:30)	16	7.84	>100	15.7	85.2	3.4	2.2	0.8	0.95

Samples collected on 03/02/2016 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NOx-N (mg/L)	NH_4-N (mg/L)
Site 2 (12:12)	18.7	6.51	72	4.01	130.9	1.9	1.7	1.3	0.27
Site 3 (11:30)	18.6	6.70	84	2.35	138.2	1.2	1.2	1.1	<0.1
Site 4 (12:39)	21.3	6.68	59	8.31	113.0	1.1	1.0	0.6	0.53
Site 7 (11:15)	20.2	6.68	85	17.1	70.4	1.9	2.0	0.4	<0.1
Site 8 (11:03)	19.0	6.62	78	5.83	74.0	1.3	0.9	0.6	0.37

Samples collected on 17/02/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NOx-N (mg/L)	NH_4-N (mg/L)
Site 1 (12:00)	21.4	8.5	96	101	108.9	4.7	2.4	1.1	1.5
Site 2 (11:40)	21.2	9.5	88	106	135.2	6.2	4.8	1.2	1.8
Site 2 storm (11:45)	No data	6.7	No data	15.4	17.9	2.1	0.9	0.5	0.3
Site 3 (11:30)	21.0	7.3	94	59.6	99.2	10.9	7.6	1.1	2.3
Site 4 (12:39)	20.8	8.2	90	72.0	123.8	12.7	9.0	1.2	3.2
Site 6 (12:20)	20.9	7.4	83	44.3	102.6	5.6	2.6	0.9	0.7
Site 7(11:15)	20.4	7.4	85	37.8	95.7	5.9	3.5	1.1	1.1
Site 8(11:03)	20.5	7.1	65	4.48	102.3	2.8	1.9	0.6	0.1

Samples collected on 01/03/2016 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (10:00)	15.8	7.2	88	0.75	115.6	2.1	1.7	1.0	<0.1
Site 2 (10:20)	15.1	7.0	92	3.55	115.5	1.9	1.4	0.6	<0.1
Site 4 (10:40)	16.5	7.1	50	5.93	103.6	1.7	1.4	0.6	0.1
Site 7 (11:00)	16.2	7.1	55	35.0	82.5	2.9	1.7	0.3	0.7
Site 8 (11:20)	16.7	6.9	59	2.26	98.7	2.1	1.4	0.5	<0.1

Samples collected on 15/03/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (18:30)	17.7	6.7	84	No data		6.3	4.6	1.1	1.5
Site 2 (18:40)	17.1	6.9	79			4.4	2.3	0.7	1.2
Site 2 runoff (18:45)	No data	7.2	No data			1.8	1.7	0.6	0.6
Site 3 (19:00)	17.3	6.9	88			46.8	46.2	1.5	13.6
Site 4 (19:15)	17.0	7.3	80			38.2	37.6	1.2	10.4
Site 6 (19:30)	17.7	6.9	64			3.8	3.5	1.0	1.3
Site 7 (19:45)	17.1	6.8	83			6.8	5.1	0.6	3.1
Site 8 (20:00)	17.0	7.2	79			1.3	1.1	0.7	0.1

Samples collected on 24/03/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (10:20)	17.2	6.1	83	26.0	80.4	2.4	2.2	0.9	0.3
Site 2 (10:35)	17.3	6.0	80	24.7	79.5	2.4	2.1	1.0	0.4
Site 3 (10:50)	17.6	6.1	84	26.1	101.7	10.6	8.8	0.9	2.3
Site 4 (11:00)	17.6	6.1	70	18.5	69.7	5.5	5.3	0.8	1.0
Site 5 (11:15)	17.7	6.1	64	13.5	70.9	4.2	4.0	0.8	1.4
Site 6 (11:30)	17.7	6.0	60	9.35	85.7	5.5	5.0	0.8	2.3
Site 7 (12:10)	17.7	6.0	55	9.32	104.9	9.0	8.7	0.8	3.1
Site 8 (12:30)	16.3	6.1	79	3.64	88.8	1.9	1.6	0.8	0.5

Samples collected on 31.03.2016 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (13:30)	16.6	7.0	65	5.26	131.8	1.8	1.5	1.3	0.3
Site 2 (13:50)	15.0	6.8	79	1.38	109.4	1.1	1.0	0.9	<0.1
Site 3 (14:15)	16.5	6.8	57	5.71	170.2	4.8	4.5	2.2	2.1
Site 4 (14:35)	17.0	7.2	91	5.39	195.5	19.9	19.6	0.9	8.7
Site 5 (14:50)	16.5	6.8	84	3.41	91.2	2.1	1.9	0.8	0.6
Site 6 (15:10)	17.5	7.0	>100	3.26	96.1	1.8	1.7	0.8	0.4
Site 7 (15:40)	20.3	7.3	>100	20.5	88.9	4.6	3.5	0.4	2.4
Site 8 (16:00)	16.0	7.2	84	3.8	93.2	2.7	1.8	1.2	0.2

Water Column Incubation Experiment

Exp. A /Week	pH	Turbidity (NTU)	Conductivity (uS)	PON (mg/L)	DON (mg/L)	TN (mg/L)	TDN (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Collect sample	6.6	4.86	288.9	1.2	16.8	34.1	32.9	1.1	15
Week 1	9.3	No Data		1.1	11.5	29.4	28.3	0.8	16
Week 2	9.7			3.9	6.9	23.7	19.8	0.7	12.2
Week 3	9.5			5.3	4.6	22	16.7	0.8	11.3
Week 4	9.8			6.1	2.4	18.1	12	0.6	9
Exp. B									
Collect sample	6.6	4.86	288.9	1.2	16.8	34.1	32.9	1.1	15
Week 1	9.5	No Data		1.2	9.3	28.6	27.4	0.8	17.3
Week 2	9.9			4	5.3	22.1	18.1	0.6	12.2
Week 3	9.6			5.9	2.4	19.6	13.7	0.7	10.6
Week 4	9.7			9.2	3.2	20	10.8	0.6	7

Wet Season

Samples collected on 07/06/2016 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (9:45)	11	8.1	64	5.30	161.9	1.3	1.0	1.0	0.1
Site 2 (10:00)	8	7.9	43	6.35	159.7	1.6	1.4	1.1	0.5
Site 3 (10:12)	10	7.6	68	2.46	120.8	0.7	0.6	1.0	<0.1
Site 4 (10:33)	7	7.4	80	7.04	96.4	<0.6	<0.6	0.8	<0.1
Site 5 (10:44)	7	7.5	55	5.22	93.2	0.9	<0.6	0.9	0.2
Site 6 (11:00)	7	6.9	78	12.2	100.0	0.7	0.4	0.7	0.1
Site 7 (11:20)	6	7.0	55	28.5	87.9	0.5	<0.6	0.5	<0.1
Site 8 (11:30)	7	7.0	80	14.4	80.6	0.6	0.7	0.6	0.3

Samples collected on 23/06/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (18:50)	11	9.8	No data	211	119.8	4.3	3.1	0.8	0.9
Site 2 (19:00)	11	9.0		131	120.2	3.5	2.9	1.0	0.7
Site 3 (19:15)	11	7.8		103	277.0	26.3	26.0	1.3	14.0
Site 4 (19:21)	11	7.5		85.9	148.8	6.3	4.9	0.9	2.5
Site 5 (19:32)	11	7.1		13.1	173.9	7.0	6.8	1.2	3.5
Site 6 (19:41)	11	7.2		9.58	146.1	2.3	2.1	1.0	1.0
Site 7 (19:51)	11	7.2		21.7	117.7	1.7	1.1	0.7	0.5
Site 8 (20:00)	11	7.7		9.35	101.5	0.6	0.2*	0.3	<0.1

Samples collected on 29/06/2016 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (12:20)	11	6.8	72	60.7	137.0	2.9	2.3	1.1	0.5
Site 2 (12:30)	9	6.9	55	22.7	158.1	4.5	4.2	1.4	2.1
Site 3 (12:45)	10	7.0	64	4.9	133.6	4.0	3.3	2.0	1.4
Site 4 (12:53)	9	6.9	59	14.9	102.3	1.3	1.1	0.9	0.6
Site 5 (13:05)	9	6.8	36	12.2	93.7	2.1	1.9	0.9	1.1
Site 6 (13:20)	10	6.7	79	14.0	85.8	1.5	1.3	1.0	0.5
Site 7 (13:45)	9	6.7	69	9.37	72.1	1.4	1.2	1.0	0.2
Site 8 (13:55)	9	6.8	91	6.99	94.9	1.4	1.2	0.7	0.4

Samples collected on 08/07/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (9:30)	8	7.8	87	26.8	77.9	3.4	1.4	1.0	0.5
Site 2 (9:43)	8	7.6	81	43.6	86.7	3.8	1.7	1.2	0.4
Site 3 (10:00)	8	7.4	83	24.8	138.2	9.8	7.7	1.5	5.7
Site 4 (10:15)	8	7.2	75	17.1	120.1	6.4	5.9	0.9	4.7
Site 5 (10:30)	8	7.0	76	16.6	99.0	3.7	2.9	1.1	2.0
Site 6 (10:40)	8	6.9	79	11.8	128.8	5.4	4.4	1.4	2.8
Site 7 (11:15)	7	6.9	78	10.9	133.9	4.8	3.9	1.7	1.8
Site 8 (11:30)	7	7.1	80	4.81	84.9	1.8	0.9	0.7	<0.1

Samples collected on 11/07/2016 – baseflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (15:20)	9	6.5	88	4.75	86.6	2.0	1.7	1.2	<0.1
Site 2 (15:30)	9	7.4	84	9.58	100.5	2.7	2.1	1.8	0.1
Site 3 (15:45)	9	7.2	65	11.6	86.2	2.3	1.5	1.2	0.3
Site 4 (16:00)	7	7.1	77	4.56	60.3	0.5	0.5	0.4	<0.1
Site 5 (16:10)	7	7.0	58	6.53	71.4	2.0	1.8	0.9	0.4
Site 6 (16:20)	7	6.8	79	7.60	101.3	3.1	2.7	1.2	1.4
Site 7 (16:45)	6	6.6	62	6.45	113.0	3.4	2.8	1.3	1.3
Site 8 (17:00)	6	7.1	96	5.84	86.2	2.2	0.6	0.4	<0.1

Samples collected on 13/07/2016 – stormflow condition

Site and sampling time	Temperature (°C)	pH	Dissolved Oxygen (%)	Turbidity (NTU)	Conductivity (uS)	Total Nitrogen (mg/L)	Total Dissolved Nitrogen (mg/L)	NO_X-N (mg/L)	NH_4-N (mg/L)
Site 1 (7:50)	10	6.9	82	33.4	61.1	2.0	1.1	0.6	0.2
Site 2 (8:10)	9	6.9	83	23.0	60.2	1.9	0.7	0.6	0.1
Site 3 (8:30)	9	6.9	89	104	57.1	3.5	1.2	0.9	0.6
Site 4 (8:40)	9	6.8	86	57.0	54.5	2.0	0.8	0.7	0.2
Site 5 (8:50)	9	6.7	76	39.4	52.7	1.7	1.1	0.6	0.3
Site 6 (9:00)	9	6.6	84	35.4	50.2	1.4	1.1	0.6	0.4
Site 7 (9:20)	8	6.7	80	28.8	53.1	2.3	1.1	0.6	0.5
Site 8 (9:30)	8	6.7	100	14.6	102.9	2.4	0.9	0.5	0.3

Appendix 2

Urea Analysis

Hill Laboratories
BETTER TESTING BETTER RESULTS

R J Hill Laboratories Limited
1 Clyde Street
Private Bag 3205
Hamilton 3240, New Zealand

Tel +64 7 858 2000
Fax +64 7 858 2001
Email mail@hill-labs.co.nz
Web www.hill-labs.co.nz

ANALYSIS REPORT

Client:	Department of Civil Engineering	**Lab No:**	1607450	SPv1
Contact:	Fabio Silveira	**Date Registered:**	28-Jun-2016	
	C/- Department of Civil Engineering	**Date Reported:**	08-Jul-2016	
	University of Canterbury	**Quote No:**	76106	
	Private Bag 4800	**Order No:**	576804	
	Christchurch 8140	**Client Reference:**		
		Submitted By:	Fabio Silveira	

Sample Type: Aqueous

	Sample Name:	WBR - Site 4 23-Jun-2016				
	Lab Number:	1607450.1				
Urea-N	g/m³	10.5	-	-	-	-

SUMMARY OF METHODS

The following table(s) gives a brief description of the methods used to conduct the analyses for this job. The detection limits given below are those attainable in a relatively clean matrix. Detection limits may be higher for individual samples should insufficient sample be available, or if the matrix requires that dilutions be performed during analysis.

Sample Type: Aqueous

Test	Method Description	Default Detection Limit	Sample No
Urea-N	Colorimetry with diacetyl monoxime & thiosemicarbazide. In-House Method.	0.05 g/m³	1

These samples were collected by yourselves (or your agent) and analysed as received at the laboratory.

Samples are held at the laboratory after reporting for a length of time depending on the preservation used and the stability of the analytes being tested. Once the storage period is completed the samples are discarded unless otherwise advised by the client.

Ara Heron BSc (Tech)
Client Services Manager - Environmental